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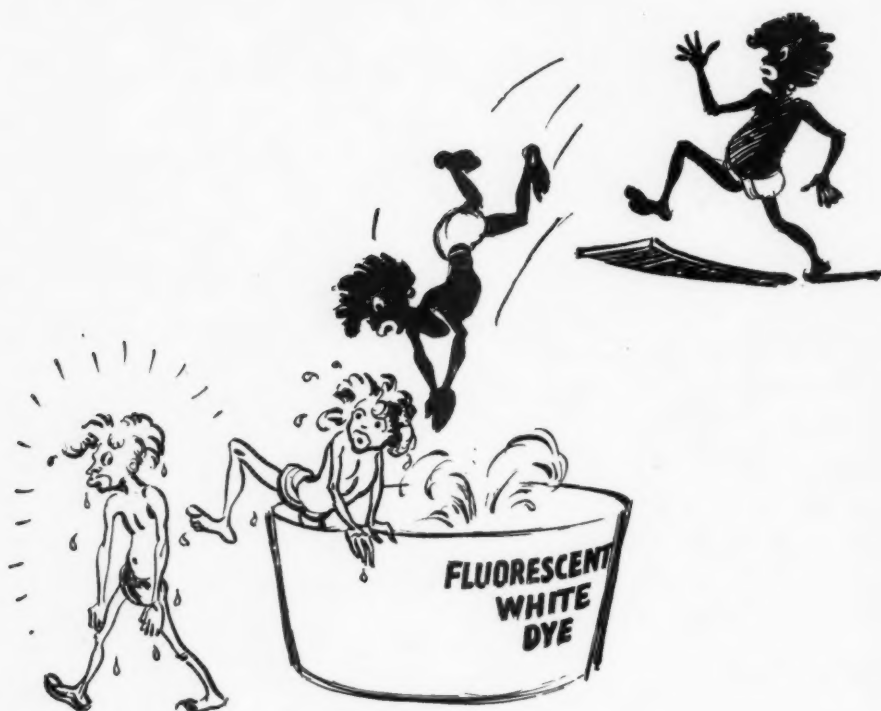
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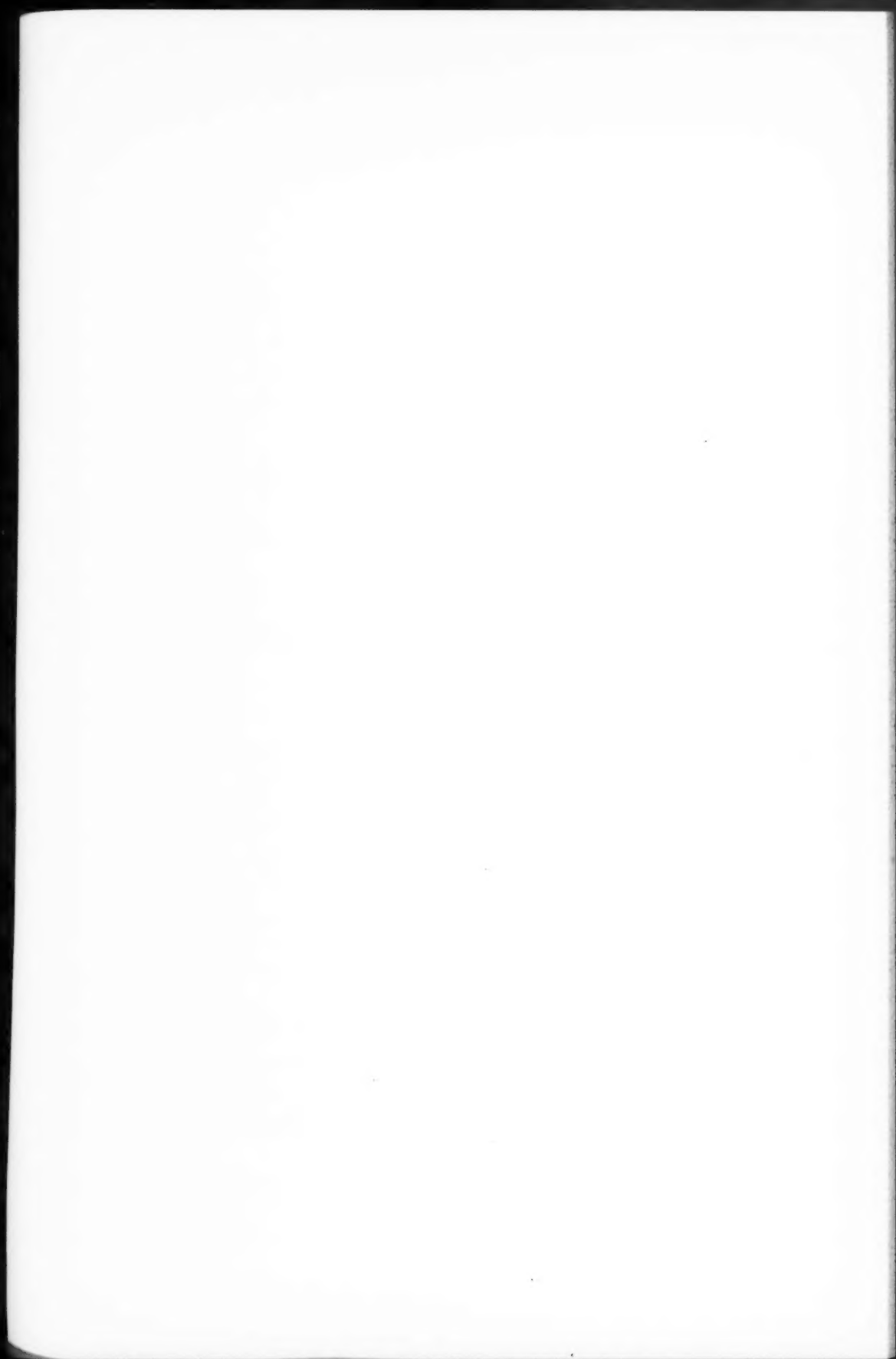


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*President of the Society of Dyers and Colourists 1946-1948*

# THE JOURNAL OF THE Society of Dyers and Colourists

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## Proceedings of the Society

### HUDDERSFIELD SECTION AND BRADFORD JUNIOR BRANCH

Meeting held at Field's Café, Huddersfield, on 8th March 1949, Mr. D. HANSON in the chair; and at the Technical College, Bradford, on 30th March 1949, Mr. J. M. GOODALL in the chair

### The Scouring of Wool with Synthetic Detergents

J. A. HEPWORTH

#### INTRODUCTION

Since the introduction of synthetic detergents the possibility of their use for scouring raw wool has been of interest to both their producers and the combing trade.

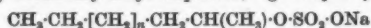
The interest of the manufacturers of synthetic detergents in introducing their products for raw wool scouring is easy to understand, since in no other section of the textile trade, and perhaps of any other trade, is the consumption of detergents so high while concentrated in so few hands. Further, but to a much lesser extent, the progressive combing is interested, since when compared technically with soap the synthetic detergents show a number of properties of interest, such as their much greater stability and solubility. However, until recent years there was little widespread interest in the actual use of synthetic detergents for raw wool scouring, since soap, in addition to being an excellent detergent with properties well understood through years of usage, was also more economic than synthetic products.

However, during the past two years the situation has changed considerably, since, while the price of soap has increased very markedly, that of the synthetic detergent has remained comparatively steady, so that in many cases now the use of soap has become more expensive than that of the synthetic detergent, and very much more interest is being shown in the possibility of alternative scouring methods.

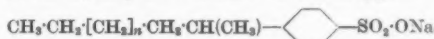
#### SYNTHETIC DETERGENTS

Before going into the question of scouring raw wool, it is of interest to consider the types of synthetic detergents available in this country. In this paper a synthetic detergent is considered to be one which is not derived from natural fats in any way, and at present there are three main types available—

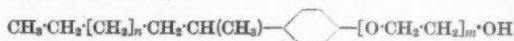
(a) secondary alkyl sulphates, e.g. Teepol type—



(b) alkarylsulphonates, e.g. Santomerse type—



(c) alkylphenol-ethylene oxide condensates, e.g. Lissapol N type—



the first two being anionic and the last non-ionic. In this country the two most important classes at present are (a) and (c), while in America the bulk of the market is held by (b). It is understood that within the next few years fairly large quantities of alkarylsulphonates will also be manufactured in this country.

The remarkable speed of introduction of these products into the general life of the community—e.g. in U.S.A. they now represent about 25%, and in this country 7–10%, of the detergents sold—has been closely connected with the development of the production of chemicals from petroleum since cheap and abundant sources of the long-chain olefins necessary were made available. It is likely, therefore, in this country, where refinery capacity is being extended by all the major petroleum firms, that production of synthetic detergents will tend to increase and that their use will become even more widespread. This tendency has prompted a much closer study of the problem of scouring wool with synthetic detergents, and some very interesting facts have been revealed.

#### RAW WOOL VARIATION

The scouring of raw wool, even though in many firms it is carried out without any scientific control whatever, is a very complicated problem of detergency. With most wools very large amounts of impurities have to be removed, wool yields of only 50% being quite common, and further, the types of impurity can vary within very wide limits even on similar qualities of wool. In addition, the scouring of merino presents different problems from that of crossbreds. Furthermore, "limey" or

slips wool, owing to the presence of large quantities of lime, causes still further difficulties.

In a recent paper by Gillespie<sup>1</sup>, it was claimed that of the total Australian wool clip, about 80,000 tons represented wool wax and 30,000 tons suint, which gives some indication of the amount of impurities which have to be removed in the scouring process. Some indication of the nature of the impurities present and the variation is shown in Tables I and II.

TABLE I  
Impurities in 64s and 70s Australian B Clear Blends

	64s	70s
	(% by weight)	
Wool fibre ... ..	61	56
Wool grease ... ..	15.2	15.9
Fatty acids ... ..	0.8	1.1
Moisture ... ..	10	9
Water-soluble impurities ...	7	5
Insoluble matter ... ..	6	13
	100	100

TABLE II  
Variation in Content of Impurities in Different Wools<sup>2</sup>  
(% of greasy fleece)

Wool ... ..	15-72
Grease and suint ... ..	12-47
Vegetable matter, burrs, dirt, etc. ...	3-24
Moisture ... ..	4-24

In addition, the different parts of the fleece show variation, and in general the suint content is low on the back and higher on the flank and belly (Table III).

TABLE III  
Yields of Wool Wax from Merino and Crossbred Fleeces<sup>3</sup>

Sheep	Percentage of Wax	
	Roots	Tips
South American crossbred ...	9.2	4.3
Australian merino ... ..	24.27	14.21
Montevideo merino ... ..	22.6	19.5

In firms dealing with such wide varieties of wools, years of experience with soap enable them in general to scour satisfactorily, the necessary adjustments in feed being made almost automatically from the appearance of the bowls or the wool, although it cannot be said that the concentrations of soda and soap used are always the most economic or in the best proportions, or that the scoured wool has a uniform grease content.

#### SCOURING PLANT VARIATION

In addition to variation in scouring requirements due to different types of wool, the problem is further complicated by the many different types of scouring sets in use. Although the most popular seem to be four-bowl sets, one meets all types from two- to six-bowl sets, and opinion is far from unanimous on the best capacity of the bowls. Further, the rate of feed of wool through the scouring set is often governed more by the requirements of the cards than by the makers' suggestions, the speed of the wool through the bowls varying within very wide limits.

When one considers all these factors, one can realise that it is not possible to give definite recipes for scouring all types of raw wool with synthetic detergents on all types of plant available. It is possible, however, to give a reasonable picture of the essential points to be watched when using synthetic detergents and to suggest certain concentrations of chemicals for trials, which can be modified to suit any particular type of plant in use.

#### SUMMARY OF ESSENTIAL POINTS

The essential factors when scouring raw wool with synthetic detergents are—

- (a) A correct concentration of electrolyte in the scouring bowls is essential.
- (b) For most economical running, the main scouring bowls must have a free soda ash content.
- (c) The correct distribution of detergent in the bowls must be maintained.
- (d) The rate of feed of soda and detergent should be just sufficient to give a steady increase in concentration during running.
- (e) The temperature of the scouring bowls must be kept sufficiently high.

#### EFFECT OF ELECTROLYTES

A number of publications on the effect of electrolyte addition on grease or oil removal from wool when scouring with synthetic detergents have appeared in the technical press from time to time<sup>3-5</sup>, and it has been shown that the addition of electrolyte when scouring with primary and secondary alkyl sulphates gives a considerable improvement in olive oil removal from wool sliver and permits a relatively large reduction in concentration of detergent. Fig. 1 and 2, taken from Aickin's paper<sup>3</sup>, show the effects of different electrolytes on the detergency of sodium secondary alkyl sulphates.

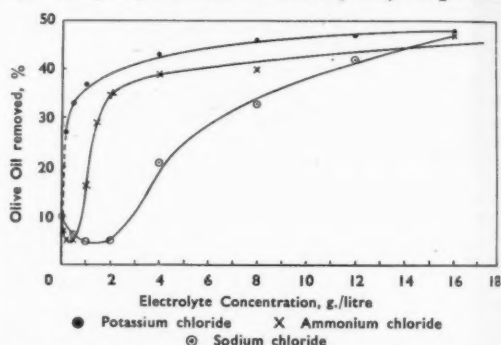


FIG. 1—Effect of Alkali-metal Halides on Removal of Olive Oil from Wool by a Solution of a Sodium Secondary Alkyl Sulphate (1.0 g./litre) at 20°C.<sup>3</sup>

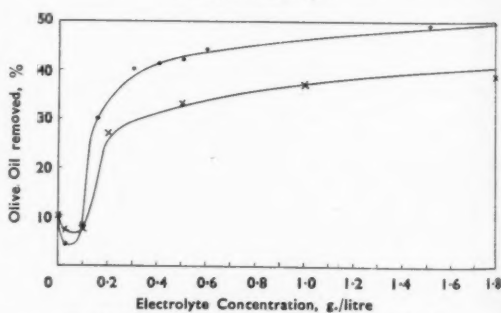


FIG. 2—Effect of Electrolytes on Removal of Olive Oil from Wool by a Solution of a Sodium Secondary Alkyl Sulphate (1 g./litre) at 20°C.<sup>3</sup>

While exactly similar curves are not obtained with all synthetic detergents, it has been shown that addition of salt considerably increases the efficiency of alkylsulphonates in removing oil

from wool, and a recent publication indicates that the ethylene oxide condensates are increased in efficiency by addition of the appropriate amount of common salt<sup>6</sup>. It is definitely established, therefore, that the increase in efficiency of grease removal by electrolyte addition is common to all synthetic detergents<sup>3-7</sup>.

It has been suggested that this improvement is due to the salt causing concentration of detergent at the oil-water interface, where, of course, it is most required. The effect, however, is not confined to synthetic detergents, but can also be demonstrated with soap, although the higher limit of electrolyte concentration is then reached more rapidly than with the more soluble synthetics and is around 5 lb. per 100 gal. Although the improvement in detergency given by electrolytes has thus been well known, its application to the scouring of raw wool was received with some doubt, and in a number of cases it was reported that the addition of electrolyte was without effect. This conclusion is now shown to be erroneous, and may have been due to the use of excessive detergent; or possibly it was not realised that the effect of electrolyte addition is less obvious if made to the first scouring bowl, where removal of free fatty acid as well as wool grease is taking place, than to the second bowl, where a relatively neutral grease is being removed. Bulk trials made under careful control have now shown without any doubt that electrolyte addition will improve the efficiency of scouring with synthetic detergents very considerably, as indicated in Fig. 3, which shows the effect of electrolyte addition in bulk working, particularly in bowl 2.

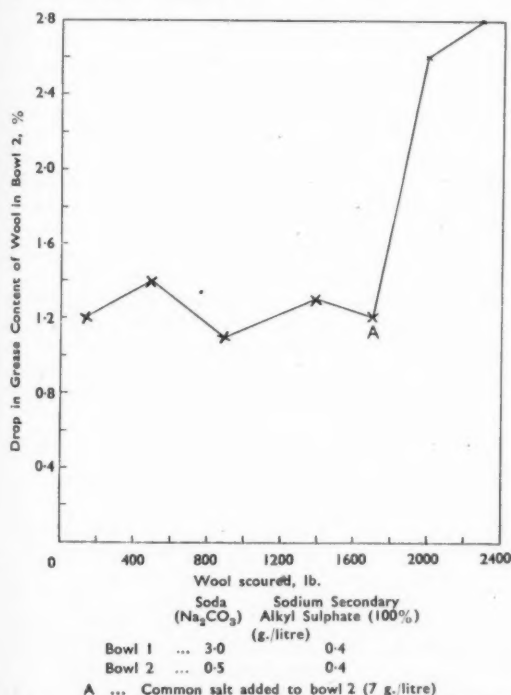


FIG. 3.—Effect of Salt Addition to Bowl 2 when scouring 64s Australian B Clear Wool

It can be seen that prior to electrolyte addition the grease removal in bowl 2 was very low, while immediately electrolyte was added it became a very effective scouring bowl, removing nearly 3% of grease. It is important to note that this effect is very difficult to obtain in any other way, and that a considerable increase in soda concentration or detergent concentration is not nearly so effective.

As indicated previously, this same effect cannot be demonstrated so effectively when electrolyte is added to bowl 1, but it has been shown that with electrolyte in both bowls it is possible to obtain very much better scouring with an overall detergent concentration of less than two-thirds of that required with no electrolyte. In fact, without electrolyte, the grease content is too high to be acceptable to most of the trade (Fig. 4).

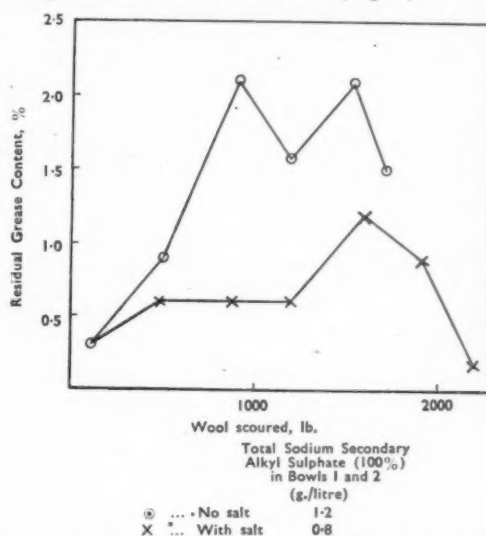


FIG. 4.—Effect of Electrolyte Addition on Residual Grease Content

There is no doubt, therefore, that when scouring raw wool with any synthetic detergent at present on the market a fairly high concentration of electrolyte is necessary, particularly if the most economical detergent consumption is required.

In addition, it is likely that, if a greasy merino type such as 64s and 70s wool is scoured without electrolyte, considerable variations in grease content of the scoured wool will be found unless very high concentrations of detergent are used.

The electrolyte most commonly recommended is, of course, common salt, and although others such as sodium sulphate, etc. can be used, it is likely that their greater cost will limit their use. Further, while it has been shown that improved results can be obtained with addition of calcium and magnesium salts in removal of olive oil from sliver, one hesitates to recommend their use or even that of hard water in scouring raw wool, since during scouring relatively large soap concentrations are formed by the action of soda on the free fatty acids in the wool, and these would form insoluble metallic soaps with calcium or magnesium salts. This would upset scouring to some extent, firstly



by removal of the electrolyte, and secondly by requiring a high concentration of detergents to keep these metallic soaps dispersed.

The optimum concentration of electrolyte varies from one detergent to another and, as with soap, there is a maximum concentration above which detergency decreases. With secondary alkyl sulphate it is recommended to use 12 times as much salt as secondary alkyl sulphate, while with the non-ionic ethylene oxide type 15-18 times the weight of detergent is suggested. (These figures refer, of course, to 100% active material, and on the material as marketed they are proportionately lower.) With the ethylene oxide type the manufacturers do not recommend exceeding a salt concentration of 1%, while with the secondary alkyl sulphates concentrations greater than 2% have no depressing effect on detergency. It is very unlikely that the maximum concentration of salt would ever be exceeded in practice, and provided low concentrations of salt are avoided, there is no tendency for the latter detergents to be "salt-sensitive". However, the use of very low salt concentrations should be avoided, since there is a tendency for detergency to be decreased under these conditions, as already shown in Fig. 1.

#### SODA ASH EFFECT

Following the résumé of the effect of electrolyte, it is worth while considering for a short time the function of soda ash in scouring raw wool. When using soap for scouring, the soda ash has the following functions—

- (1) To maintain the pH sufficiently high to keep the soap functioning at its maximum efficiency
- (2) To neutralise the free fatty acid present in the wool grease, so forming further soap
- (3) To act as an electrolyte to increase the detergent power of the soap.

When soap is used for scouring wool, variation in pH can affect the detergency to a very marked degree, particularly when the pH is allowed to fall. For instance, if it is allowed to fall even as low as 8, the grease content of the wool can actually increase after passage through the scouring bowl, owing to deposition of fatty acid from the soap in the wool grease. On the other hand, increase in pH above 8.5 increases the detergent power of soap considerably.

With synthetic detergents, however, the function of soda ash is rather different. As is well known, the scouring efficiency of synthetic detergents does not vary nearly so widely with pH as does that of soap, and the synthetic detergents mentioned still have some efficiency even on the acid side of neutrality. Consideration of this fact alone would indicate that it should be possible to scour raw wool without soda addition at all. This has been done, but in all cases the amount of detergent used is very much increased, for three reasons—

(a) Synthetic detergents are generally more efficient when used under alkaline conditions, although the variation in efficiency with pH alterations is small (Fig. 5).

(b) Without soda the free fatty acid in the wool grease remains unsaponified, and since a normal 64s Australian merino may contain up to 1% free

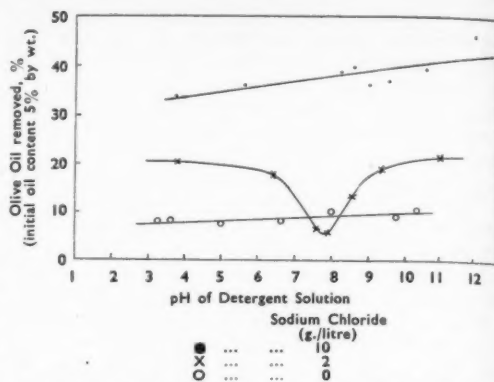


Fig. 5—Effect of Variations of pH on the Removal of Olive Oil from Wool by Sodium Secondary Alkyl Sulphate Solutions (1 g./litre)<sup>2</sup>

fatty acid, the loss of this potential soap is quite large when one considers that few combers use more than 2% soap on the weight of greasy merino scoured.

(c) With the sulphate or sulphonate type of synthetic detergent there is considerable adsorption of detergent under neutral or slightly acid conditions.

For the most economical scouring, therefore, it is necessary to use soda along with detergent and electrolyte, and it will be found that, where the minimum of soda possible is used with soap, very little saving in soda is possible on replacing soap with synthetic detergent.

The reasons for this are easy to see when one again considers the function of the soda and also what happens to it during the scouring of wool. It has been decided that sufficient soda must be used to saponify the free fatty acid present in the wool grease to obtain the benefit of the soap thus formed in the scouring process, so no saving in soda for neutralising the grease can be expected. However, the amount required for this is relatively small, being only of the order of 3-7 lb. per 1000 lb. of greasy wool, while the normal soda consumption is around 20 lb. per 1000 lb. of greasy wool. Investigation under careful control confirms these figures, and we have shown that, if wool is scoured through 850 gal. of a 2 lb./100 gal. soda solution at 130°F. with an immersion time of 3 min., then after 1800-2000 lb. of wool no free soda is present (Fig. 6). Further, to maintain a free soda concentration of 3.5 lb./100 gal. under the same conditions

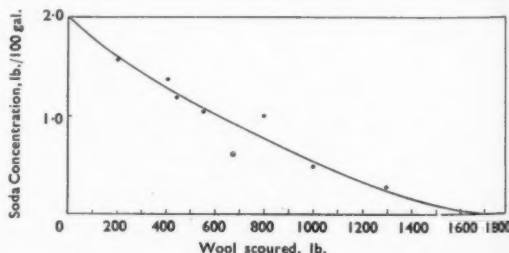


Fig. 6—Drop in Soda Concentration when scouring 64s Merino without Soda Feed (850 gal. of solution in bowl 1)

a feed of 20 lb. of soda per 1000 lb. of greasy wool is necessary.

It is evident, therefore, that the main factor in soda consumption is not the neutralisation of the free fatty acid but another. This is the soda adsorbed by the wool, which is very much greater than the amount used in neutralisation of free fatty acid. Unfortunately, the adsorption by the wool takes place preferentially, and if scouring is to be carried out under alkaline conditions take-up of alkali by the wool must occur. Thus one cannot expect to achieve much saving of alkali when using synthetic detergents unless the amount of detergent used can be increased considerably.

The adsorption of alkali by wool during scouring is a factor which has received much thought, since, unfortunately, it is not possible to wash out in the rinse bowls all the alkali taken up in the scouring bowls, and it is said that if excessive alkali is taken into the drier, then the wool is yellowed. Unfortunately again, most of the factors tending towards improved detergency increase the alkali adsorption, since this adsorption increases with increases in (i) pH, (ii) electrolyte concentration, (iii) temperature, and (iv) scouring time. It is therefore essential that the soda concentration should be kept to the minimum required for safe scouring, and if possible any free soda addition should be limited to the first bowl, where the rapid formation of bicarbonate during scouring gives a strong buffering action. In a number of cases the very considerable increase in detergent consumption is preferred to using an alkaline scouring method, particularly for mohair scouring. The safe alkali content for scoured wool can be accepted as approx. 0.4% expressed as NaOH.

The total alkali required for satisfactory scouring depends very largely upon the scouring method adopted and the type of machine available. With three-bowl sets, where very efficient scouring in the first bowl is essential and fairly high concentrations of soda have to be used, the soda consumption will tend to be greater than with a four- or five-bowl set, in which it is possible to use the first bowl as a steep bowl and so cut down the overall concentrations required. Where self-cleaner systems are used on the first bowl, if reasonable chemical costs are to be expected, it is essential to use this as a steep bowl, with no feed other than sufficient soda to keep the pH at 8.5-9, since it has been shown that grease removal is best at this pH with suint liquors.

#### DETERGENT EFFECT

Finally in this section we have the detergent itself. The function of the detergent in raw wool scouring, whether soap or synthetic, is primarily to remove and emulsify the grease present, since the bulk of the dirt and sand present is embedded in the grease and will come away with it. Mill-scale running both in this country and in America has shown that synthetic detergents are quite capable of removing the wool grease and keeping it emulsified and that the final colour of the scoured wool is good, with a grease content well below the 0.8% normally required.

With the alkyl sulphates and alkarylsulphonates it has been suggested that there is a considerable

amount of adsorption of detergent by the wool fibre during running. A study of the drop in concentration of alkyl sulphate in the different bowls of a scouring set shows the interesting fact that, with similar nip between each, the rate of drop of concentration is practically negligible in bowl 1, and in bowl 2 is less than in bowl 3, and that this effect occurs in spite of the fact that the time of immersion in bowl 3 is less than in either bowls 1 or 2. Fig. 7 shows this difference effectively. Within the limits of these trials it appears that the rate of adsorption increases with increased time in the solution, even under conditions in which all baths are alkaline, and in fact contain free soda ash.

These data indicate that it will be unnecessary to feed alkyl sulphate into bowl 1, and that the feed into bowl 3 will need to be proportionally

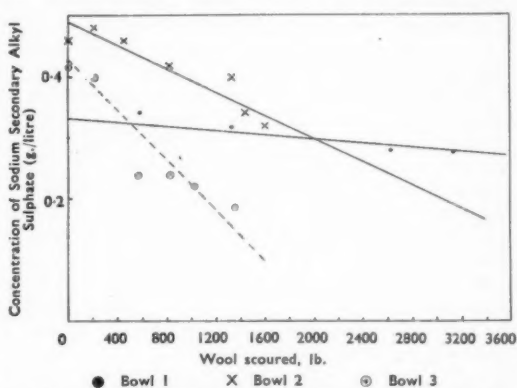


FIG. 7—Drop in Concentration of Sodium Secondary Alkyl Sulphate when scouring 64s Merino

greater than the feed into bowl 2 to compensate for the increased loss. The total adsorption of alkyl sulphate by the wool is not excessive, however, since the adsorption is reduced considerably with increase in pH (Fig. 8).

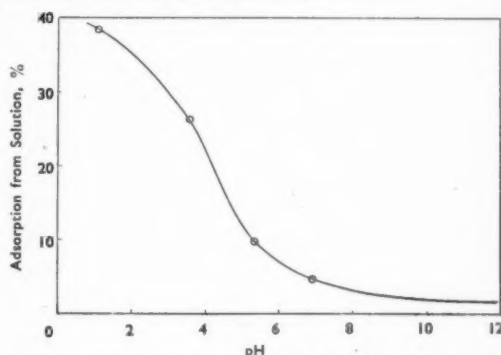


FIG. 8—Adsorption of Sodium Lauryl Sulphate by Wool as a Function of pH

#### TEMPERATURE EFFECT

Little need be said about temperatures to be used. When scouring with synthetic detergents and soda the usual temperatures of soap scouring can be employed, and as with soap it is essential to keep bowl 1 at around 130°F., with the other bowls gradually dropping in temperature to a final



bowl of 110–115°F. With neutral scouring with non-ionics it has been suggested that higher temperatures than usual can be employed, and 160°F. in bowl 1 has been recommended.

#### RECOMMENDATIONS FOR BULK WORKING

The following discussion on the use of synthetic detergents on a large scale is confined to secondary alkyl sulphates, but the comments are probably applicable to all synthetic detergents, although the concentrations required will, of course, differ very considerably.

From the facts outlined above, it can be seen that for the most economical scouring results with synthetic detergents the addition of both soda and electrolyte is necessary. However, the distribution of soda, detergent, and electrolyte between the different bowls is also of great importance. To some extent this distribution must be determined by the type of machine available, as one would expect, since the smaller the number of scouring bowls the greater the percentage of grease removal necessary in the earlier bowls. For instance, with a three-bowl set scouring 64s and 70s merino, to be certain of final grease figures of less than 0.8% it is essential that the wool leaving bowl 1 should not contain for long runs more than 3.0% grease; while with a four-bowl set under certain conditions the wool can leave bowl 1 with up to 7% grease, although it should not leave bowl 2 with more than 2%. When working with a three-bowl set, therefore, there is great strain on both bowls 1 and 2. Accordingly higher detergent and soda concentrations are necessary than with sets containing more bowls, and this does to some extent increase the overall chemical consumption. With a four-bowl set the most economical method is to use the first as a steep bowl containing only a blow-back liquor with just sufficient soda feed to keep it at pH 9, followed by a scour in bowl 2. Bowls 3 and 4 will then be used almost as rinse bowls, and will act as a buffer against any scouring errors in the earlier bowls. With a five-bowl set, the scouring required in bowl 2 can be reduced, allowing still further reduction in chemical consumption.

#### STARTING CONCENTRATIONS

Since in scouring raw wool for the combing industry the object is not to remove the whole of the natural grease, but to leave in amounts of 0.6–0.8%, it is necessary to arrange the starting concentration, distribution, and feed of detergent, soda, and electrolyte so that overscouring at the start of a run and underscouring at the end are avoided. It is important that overscouring in bowl 1 should be avoided, and it is preferable for the wool to leave bowl 1 with at least 3–4% grease still present from the very start of scouring, depending upon the plant available.

Using blow-back liquors, the concentrations of secondary alkyl sulphate, soda, and salt given in Table IV have been found sufficient in bulk scouring to start up when scouring 64s and 70s merino. Normally the procedure each shift is to start up from blow-back liquors, and only once each week is scouring started from clean liquors. It is an interesting fact that higher concentrations of

detergent and soda are required when starting up from clean liquors than from blow-back, as indicated by the concentrations shown in Table V for starting up with secondary alkyl sulphate as detergent when scouring merino in a four-bowl set. This may be due to absence of suint and soap formed by neutralisation of fatty acid in the wool grease. When starting up with synthetic detergents after using soap it is likely that still higher concentrations of synthetics may be required.

TABLE IV  
Average Concentrations required when scouring Merino Wools with Sodium Secondary Alkyl Sulphates using Blow-back Liquors

No. of bowls	Soda (g./litre)			Salt (g./litre)			Alkyl Sulphate (100%) (g./litre)		
	3	4	5	3	4	5	3	4	5
Bowl 1 ...	3.5	1.0	1.0	—	—	—	0.35	0.3	0.3
Bowl 2 ...	0.5	2.5	2.0	7.0	4.0	3.5	0.55	0.375	0.3
Bowl 3 ...	—	0.2	0.2	—	5.0	4.0	—	0.3	0.25
Bowl 4 ...	—	—	—	—	—	—	—	—	0.075
Bowl 5 ...	—	—	—	—	—	—	—	—	—

TABLE V  
Difference in Concentrations required between Blow-back and Clean Liquors

	Soda (g./litre)		Salt (g./litre)		Alkyl Sulphate (100%) (g./litre)	
	Blow-back	Clean	Blow-back	Clean	Blow-back	Clean
Bowl 1 ...	1.0	1.5	—	—	0.3	0.3
Bowl 2 ...	2.5	3.0	3.5	4.0	0.375	0.4
Bowl 3 ...	0.2	0.5	4.0	4.0	0.3	0.45
Bowl 4 ...	—	—	—	—	—	—

#### FEED

As indicated previously, while these concentrations are sufficient to give good scouring at the start of a run, it is essential to feed both soda and detergent, and with some machines electrolyte, if good results are to be maintained. With a three-bowl machine it has been found that it is necessary to feed soda only into bowl 1 and detergent only into bowl 2, since the suint and soap build-up in bowl 1 is sufficient to keep the gradually increasing concentration of wool grease in that bowl emulsified, and there is sufficient carry-over of soda from bowl 1 to keep bowl 2 slightly alkaline. On a four-bowl set, where the most economical method is to use bowl 1 as a steep bowl, soda feed is necessary only into bowls 1 and 2, and sufficient soda should be added to these to keep bowl 1 at pH 9 as indicated previously and to keep bowl 2 at pH 10–10.5, while detergent feed is necessary only into bowls 2 and 3. Where a self-cleaner system is operating, the feeds will need to be increased to compensate for the loss of liquor. It is not recommended to use a self-cleaner system on a three-bowl set unless it can be adjusted to give a very low liquor loss, since with a three-bowl set the concentration of chemicals in bowl 1 is very high.

TABLE VI  
Average Feed required per 1000 lb. of Greasy Merino Wools on Scouring Plants without Self-cleaning Systems

	Soda (lb.)	Alkyl Sulphate (100%) (lb.)
3-BOWL SETS		
Bowl 1 ...	15–20	—
Bowl 2 ...	—	1.2–1.8
4-BOWL SETS		
Bowl 1 ...	6–10	—
Bowl 2 ...	3–5	0.6–1.1
Bowl 3 ...	—	0.6–1.1

In scouring 64s merino, some indication of the feed necessary on different types of scouring sets is

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Table V  
phate as  
bowl set,  
and soap  
the wool  
deter.  
all higher  
required.

ino Wool  
low-back

Sulphate  
(00%)  
(litre)  
4 5  
3 0.3  
0.75 0.3  
3 0.25  
— 0.075

Sulphate  
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given in Table VI. The figures refer to 1000 lb. of greasy wool, but this is purely for simplicity, and no more than 500 lb. should be scoured without feeding. In fact, continuous feeding is the most desirable method, since then wide variations in concentrations are avoided, and it is possible to scour at lower detergent and soda concentrations. Since the only loss of electrolyte is through the nip or self-cleaner, it will be in general unnecessary to feed salt, except when using a machine with a self-cleaner or other system where relatively heavy liquor losses occur.

#### CROSSBREDS

So far, the discussion has been more or less confined to the scouring of finer-quality wools, since it is accepted that merinos are more difficult to scour than most crossbred qualities, and if the synthetics will scour merinos to a low grease content, most crossbred qualities should offer no difficulty. This has been found to be the case, and in general scouring costs can be reduced by 30-40% for crossbred qualities compared with merinos using similar recipes.

#### SLIPE

In scouring "limey" or "slipe" wools, the synthetic detergents, owing to their greater stability to the calcium salts present, show to great advantage when compared with soap. It is possible with synthetic detergents to use almost the same recipes as for a sheared wool. This means a considerable economy in detergent compared with soap, and where a number of different blends have to be scoured on the same set, a very much safer and less complicated running.

#### WOOLLEN TRADE

Up to this stage, consideration has been confined to the scouring of wool to a grease content of below 0.8%, as required for the combing trade. In the woollen trade, however, quite a large number of vertical firms prefer to scour to 2-3% of grease, provided the wool is otherwise clean. In this way they find that it is possible to economise in oil added for carding, and in place of 10% on a perfectly scoured wool they can use 6-7% on a wool scoured to 2-3% of grease. On a woollen card wool prepared in this way cards quite satisfactorily, and in many cases it is preferred as being less "wild", in addition to saving 30% in oil.

To scour the wool clean and at the same time retain a definite amount of wool grease of 2-3% is rather difficult with soap, but it has been found to be relatively easy with sodium secondary alkyl sulphates. By omitting electrolyte addition in bowls 2 and 3, as seen earlier, very little grease removal takes place below 2%, unless excessive quantities of detergent or alkali are present. Using a normal recipe in bowl 1, therefore, to give the usual 3-4% grease content on leaving this bowl, and working without electrolyte in bowls 2 and 3, it is easy to keep a grease content of 2-3%. It is a fact that wool scoured in this way looks surprisingly clean, and this in the early days caused a lot of trouble.

Having now shown that the synthetic detergents can be regarded seriously as alternatives to soap,

the difficulties likely to be encountered when synthetics are first used should be considered, since most changes are accompanied by some new problems. As indicated earlier, the use of soap in scouring is based on years of experience, and on changing to a synthetic this experience must be to a large extent discounted, since the appearance of the scouring bowls will be very different. This is due to two facts, the first being that soap lather is thicker and heavier than the synthetic detergent lather, and further the presence of lather on a synthetic detergent liquid does not necessarily indicate that it is scouring as it should. However, particularly with the sulphonate or sulphate type of product, estimation of detergent and soda content in the liquors together with pH determination are quite easily carried out, so that until the bowl minders have the "feel" of the synthetic detergent, the process can be readily controlled analytically.

Again, to a lesser extent, the wool has a rather different appearance, being in general more lofty. This loftiness may be rather deceiving until one has experience with synthetics, since there is a tendency to underestimate the grease content. However, after a week's run the difference should be understood, and the bowl minder should be able to judge in his usual way whether the wool is clean or not.

Finally, there is the question of effluent treatment when synthetic detergents are used. Here it must be stated that the author's experience is confined to secondary alkyl sulphates, but all synthetics, owing to their increased stability, are likely to call for some modification in effluent treatment. Under suitable conditions works' effluents containing sodium secondary alkyl sulphates will crack with acid to give an effluent containing very little grease, but these conditions are different from those under which soap effluents will crack. To deal fully with this matter would take too long, but in brief, it has been shown that, where a wool-scouring effluent containing sodium secondary alkyl sulphate can be cooled down to around 25°C., it will crack quite readily with acid. If in addition a small percentage of soap is present, the resulting effluent will be even better. These remarks, of course, refer only to a concentrated works' effluent and not to regional sewage treatment, where rather different factors operate.

It is hoped that this review of the recent progress in scouring raw wool with synthetic detergents has indicated that they do present new possibilities in the industry. One or two problems connected with the use of synthetics still remain to be solved, but the fundamental fact that it is possible to scour any type of raw wool clean and to the grease content required by the trade, at a reasonable cost, has been established. No comments have been made on the influence on the physical properties, since this problem is at the moment under investigation, but it can be said that so far very little difference in properties has been found.

In conclusion, the author would like to express his thanks to the Principal of the Bradford Technical College for permission to carry out many of

the trials described, and to members of his staff for their valuable assistance during the investigations. Acknowledgment should be made also to Messrs. Shell Chemicals Ltd. for permission to publish this paper, and to the author's colleagues, Messrs. H. Carter, M. Elton, S. W. Farrington, and H. C. Tait, for assistance in planning the investigations and carrying out bulk trials.

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## MANCHESTER SECTION

Meeting held at the Technical School, Bury, on 4th February 1949  
Mr. N. HAMER in the chair

### Warp Dyeing

G. S. MARR

In introducing his paper the Lecturer said—  
"I feel I should commence in apologetic vein. By contrast from the distinguished lecturers customary at this scientific Society my only qualification lies in my intimate connection with that little publicised field of textile activity, warp dyeing, being in fact just a practical warp dyer. Consequently it was not without considerable hesitation that I accepted the Society's invitation, and not before the added and somewhat ambiguous encouragement, that my paper would be welcomed, at any rate, as a change in the Society's diet. Despite the foreboding I now feel on seeing so many practical faces before me, I can only hope this catholic spirit will prevail this evening."

For some reason, or lack of any, warp dyeing has never received much publicity in technical circles, but despite this grave omission the practice of warp dyeing is of very considerable importance to Lancashire. Some twenty years ago I was informed by knowledgeable persons in the textile trade, not of course practical dyers, that warp dyeing had had its day and was rapidly approaching redundancy; but this opinion was nothing more than the misconceived reflections of the additions to warp dyeing technique and the inadequate appreciation of the importance of warp dyeing, for in fact, Phoenix-like, the warp dyer rose from these premature ashes with additional plumage and increased vigour, to such purpose that nowadays the activities of the competent warp dyer are considerably extended, and his services increasingly sought.

Really the term "warp dyer" is something of an understatement, for in addition to the multi-processes of mercerising, bleaching, dyeing, sizing, and proofing, preliminary processes of yarn conversion from non-warp package to warp package form, and subsequent processes of conversion of the dyed and invariably sized warps to back beam or to weaver's beam, all ready for weaving in the loom, are frequently involved. Provision is made also for weft warps—which sound something of a paradox—to be wound to pirn package all ready for putting in the shuttle. So the warp dyer, who now dyes rayon and speciality yarns as well as cotton, spans a very considerable gap between the spinner and the weaver, and by a comprehensive

service accommodates the frequent ill adjustments of supply and manipulates them to the requirements of the cloth manufacturer.

Dyeing direct in the warp form (be it ball warp, cross-ball warp, or beam warp) eliminates intermediate winding processes and also accommodates all practical yarn weight requirements.

This comprehensive yarn service to the textile trade is not without its adversity, of course.

In addition to the tremendous advantage of this characteristic comprehensive adaptability, which serves the cloth manufacturer who is without "preparation" facilities (i.e. dressing, beaming, taping, and winding plant) equally well as the manufacturer possessing these facilities, there are the technical advantages by which in certain cloths which demand unbroken continuity of shade, such as gabardines, coutils, and various other "solid" colour or "self" colour cloths, the best results alone can be obtained; and dyeing direct in the warp form ensures a minimum of yarn wastage.

The warp dyer commences wet processing with yarn in either—

- (1) The crossball or cheese package (synonymous terms)
- (2) The ball warp package
- (3) The beam warp package.

Generally speaking, the crossball package, in which the warp in closed draft is cross-wound on spool in cylindrical form, provides for requirements of warp length and whereby the number of ends of yarn in the warp is limited to a maximum of around 600-700; whereas the ball warp, coiled in closed draft like a ball of string, provides for requirements of maximum number of ends of yarn in the warp, as many as 2000 or so, and whereby the length of warp is limited to a maximum of something around 1000-1500 yd., generally speaking. I emphasise the phrase "generally speaking", for any attempt to rationalise the ramifications of textile manipulation must always be carefully qualified: yarn counts and particular requirements are very variable factors.

The beam package, where the warp in open draft is wound on a spinner's flanged beam 54 in. between the flanges, like the crossball is limited in the number of ends to a customary maximum of

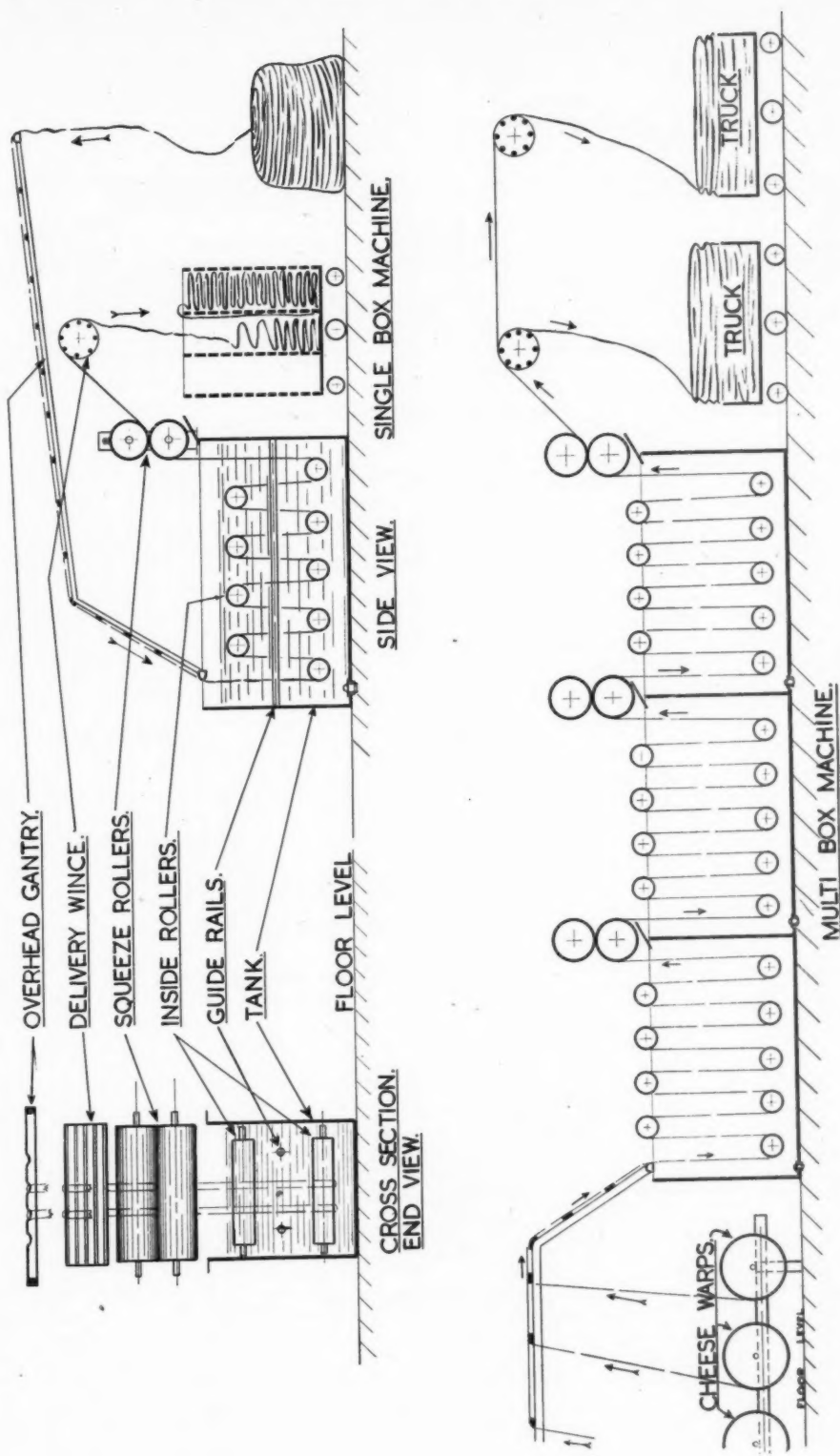


FIG. 1—Open-box Warp-dyeing Machine



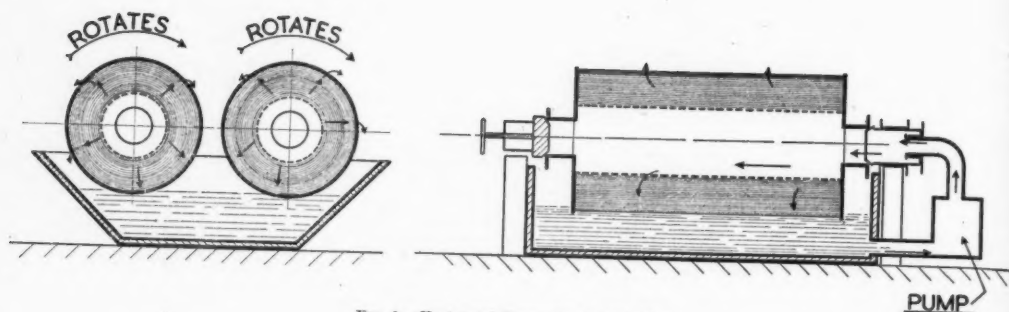


FIG. 2—Horizontal Beam Dyeing Machine

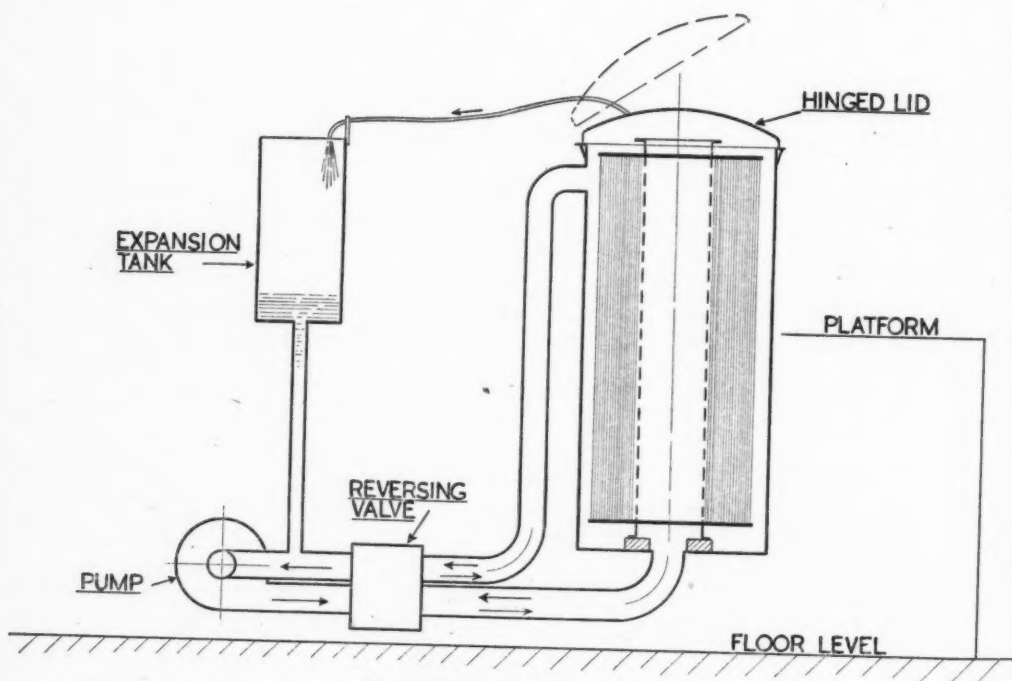


FIG. 3—Closed Beam Dyeing Machine

about 400-600, and provides for a length of warp of approx. 10,000-15,000 yd. according to yarn counts.

Whereas a ball warp may not frequently exceed about 100 lb. in weight, a crossball warp may be as much as 250 lb., and a warp on beam for dyeing may be 150-250 lb. according to yarn counts.

Both ball warps and crossball warps are carefully leased by the spinner to provide manipulative control during the processes of dressing and beaming prior to weaving: this is most important, for any ball warp or crossball warp without these lease bands is virtually so much waste yarn.

The crossball carries an "end-and-end" lease band at each end of the warp, and usually also at about 500- or 1000-yd. intervals throughout the warp length. This end-and-end lease, as its name implies, separates and maintains the original position and identity of each individual end of yarn in the warp as made by the spinner, and is the key to the handling of the warp in the open draft in subsequent dressing, beaming, etc.

The ball warp usually only carries an end-and-end lease band at each end of the warp, but having been built up on a warping mill carries also a "half beer" lease, which is a preliminary lease band at the beginning end of the ball warp separating 10 or 20 ends at a time for the purpose of quick counting for subsequent splitting off and dressing purposes.

In the case of the warp on beam, which is in fact a sort of permanent open-draft form of warp package, an end-and-end lease band is readily picked across the open draft to serve practical purposes, although it may not accurately conform to the original setting of the yarn.

For many years warp yarn in the crossball and ball packages was wet-processed entirely on the principle of passing the yarn at length through the liquor by the use of single- or multiple-box machines, which are in effect either single tanks or boxes or series of such in succession, containing inner guide or traverse rollers and upper headstock squeeze rollers. The expression "passing the warp yarn at length" should not be taken too precisely, for it does not preclude various methods of "doubling up" the warps to shorten their length and to increase their working thickness for both economic and technical reasons. This optimum assembling of the warp yarn may be a preparatory processing of the yarn in the natural grey state as received from the spinner, or it may be manipulated during an initial run through a wet-process machine.

Latterly, however, much has been done to reverse the original dyeing principle and to develop the method of passing the liquor through the yarn under pressure, and in this system warp yarn on beam is transferred to a perforated dyer's beam and immersed in the dye liquor, which is made to circulate through the yarn mass.

As is always the case when there is more than one method of achieving an object, contending opinion exists as to the comparative merits of the several processes of warp dyeing: I feel, however,

that, just as there was much unbalanced anticipation at the prospect of rayon superseding cotton when the former fibre became a commercial entity, so there has been unnecessary contention about the various methods of warp dyeing, and in my opinion the sober truth of the matter is that, just as rayon and cotton have come to be regarded as complementary fibres, so the various methods of warp dyeing are complementary and should be used as such. The progressive warp dyer realises this and makes provision accordingly.

Some of the few published accounts of warp dyeing are rather surprising. Thus, in one very up-to-date and excellent treatise, on dyeing, reference is made to the respective purposes of single- and multi-box warp-dyeing machines, and the impression given that the multiple-box machine is used for the purpose of reducing the number of runs that would be required with a single-box machine, *but* that the dyer has less control, in consequence of which use of the multiple-box machine is limited to the dyeing of dark shades, where differences in shade are not discernible and then only with the more simply working dyes.

Now, on the contrary, whilst the mechanical principles of the ordinary open warp-dyeing machine, through which the warp yarn is passed at length, are comparatively simple and have long been known, no other method of yarn dyeing enables such large weights of yarn to be dyed in one batch or with such regularity in continuity of shade. This is a very important point and explains why this method finds such extensive application in the dyeing of stock warps, i.e. batches of warps from which manufacturers take, repeat, and make up their design requirements with confidence in continuity of shade.

This is the only satisfactory method of yarn-dyeing gabardines, both warp and weft warps, in which type of trade occur both delicate and dense sulphur shades requiring considerable control. It is the only satisfactory method of yarn-dyeing coutils, again both warp and weft, which trade also is characterised by the most delicate shades. Both gabardines and coutils demand a very high standard of shade accuracy and continuity, and these cloths readily reveal the minutest variations in shade.

Azoic shades have long been dyed on multiple open-box machines involving continuous and consecutive naphtholation and development.

Further, vat shades of all types, both delicate and dense, have long been dyed by this method with every satisfaction.

The above misconceptions are, however, perfectly understandable, for warp dyeing is part science, part art, and part craft; and maybe it is partly the fault of the warp dyer himself that more is not known of his very considerable and important work, and partly of the difficulty of giving concise expression to his craft.

Hard-and-fast processing procedure is not characteristic of warp-dyeing technique, and procedure varies considerably according to the type of trade involved, the facilities of the plant concerned, the whims of the customer, and the notions of the

dye—or *vice versa*. Although preliminary wet processing of the yarn prior to dyeing is not necessarily a constant feature, the wet preparation may be either a kier boil, an open warp machine boil, or a speciality wetting-out treatment.

Similarly, the dyeing operation itself varies considerably. The dyer must judge the necessity for using a single-box or a multi-box machine, and considerations of total weight of yarn involved, density of shade, and quality of dye are all involved in making a decision. Possibly no two warp dyers are just alike in their approach to any particular job, but quite obviously a large batch of yarn for vat dyeing would not be a happy choice for processing through a single-box machine of, say, 100 gall. capacity, whether the shade be delicate or dense. There are (if we do not forget to add "generally speaking"), however, two principles of operational control which might be acceptable as standard.

One is the method of passing a comparatively short run of yarn through the dye liquor without replenishing the liquor during the running of the yarn. In this method the liquor is prepared to give a commencing shade of, say, about one-third to one-half the shade density required, when the warp run tails off during the run. After the first run the dye liquor is replenished and the yarn run through a second time, the end last out of the dye liquor in the first run being the end first through the replenished dye liquor, so that the net effect is a balancing of colour density. A further run or runs, with or without replenishment of the liquor—each run being in the reverse direction of the warp—levels the warp run to the desired shade. This method is of somewhat limited use, depending on the amount of yarn involved, the substantivity of the dyes employed, and the type of shade required; nor is it suitable for compound process runs.

The other is the method of constant feed during the run, where the object is to produce an unvarying continuity of shade during each run until the final desired shade is obtained. This requires considerable skill on the part of both the head dyer, who selects the dye and gives process instructions, and of the machine man, who manipulates and controls the progress of the dyeing; in this combination of science, art, and craft, one might say that the head dyer supplies the science, the machine man the art, and the manager the very crafty background.

A full range of dye qualities can be applied using the open warp-dyeing machine, e.g. direct, sulphur, developed, basic, vat, and azoic.

In a multibox machine, compound dyeing processes such as diazotising and developing, and naphtholating and developing, can proceed consecutively as the warp yarn runs through the machine.

An early washing of the dyed yarn is invariably desirable, and may be a part of the run through a multibox machine or an entirely separate run through a finishing machine, e.g. in chroming sulphur colours or soaping vat colours.

Throughout these operations the squeeze rollers in the upper headstock express the liquor from the

yarn back into the machine, thereby preventing excess liquor passing from one compartment to a following liquor, and finally leaving the yarn in a fit state for piling and handling in the trucks that receive it out of the machine.

The comparatively recent method of pressure dyeing warp yarn on the beam differs fundamentally from the open warp machine dyeing in that the liquor is passed through the yarn mass not the yarn through the dye liquor; in that the period of contact between liquor and yarn is very much longer; and also in the limiting factor of the yarn capacity of the machine.

In this method, an accurate predetermination of the recipe required is desirable, so that the shade may be obtained without recourse to subsequent adjustments. Surplus liquor is extracted by centrifuge or vacuum.

The pressure dyeing method is not of such wide application as the open warp machine method of dyeing: the enclosed design of these pressure dyeing machines is a limiting factor in respect of the yarn load, and the different qualities of dye are not all suited to the conditions; direct and vat dyes predominate.

After dyeing and drying, warp yarn is mostly sized; but a word about drying. In the case of crossball warps and ball warps drying over steam-heated cylinders is mostly the practice, although systems of hot-air or stove drying are also operated. These drying cylinders, fondly known as "cans", approx. 12 ft. long  $\times$  2 ft. in diameter, are arranged in batteries of about 16-24, and the warp draft to be dried is passed through the battery in such a way that it passes over or under every cylinder in the battery, in direct contact, losing moisture progressively. One passage or lap round the cylinders is insufficient to dry the closed yarn draft, which is arranged so as to pass continuously round the cylinders for, say, five to eight separate and laterally consecutive laps. According to the size of the cylinders in the battery, i.e. their drying capacity, there may be provision for two, three, or four separate courses of laps, each course, of, say, five to eight laps.

The cylinders, which work at an internal maximum steam pressure of 10 lb./sq. in., are kept permanently threaded with bands of one description or another in order conveniently to attach and lead round the cylinders the warp proper to be dried.

In the good old days, of so very long ago, before the development of the dye ranges with which we are now familiar, and when the warp dyer's repertoire was little more than direct skies, blues, pinks, helios, blacks, Benzo Red, Indigo, and Cutch, the successful warp dyer made his name more by virtue of his ability to size the warps in a satisfactory manner rather than by dyeing them; and although the quality of the applied dyes has become so important nowadays, the quality of the sizing is no less important than hitherto; indeed it is paramount. All warps, of course, are not sized alike, considerable differences being required according to the counts of yarn, the weaving conditions, and the type of cloth; but to state the



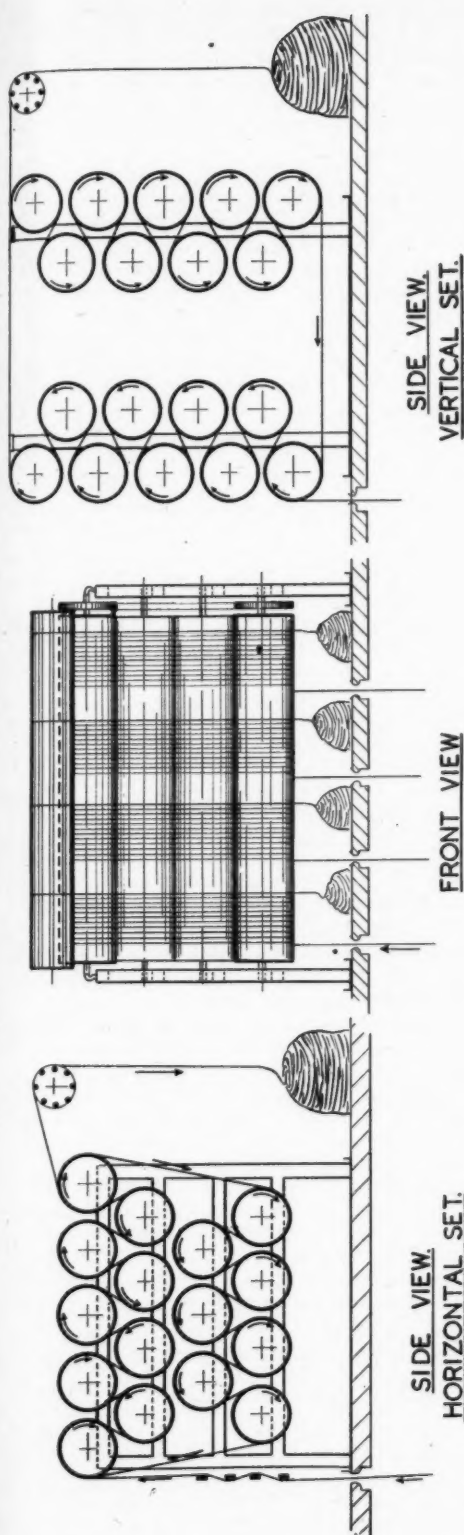


FIG. 4—Drying Cylinders

overall desideratum, I think most cloth manufacturers would agree that a sized warp must be "mellow" enough to open readily, so that its individual ends of yarn run freely in either back beaming or dressing, and each individual end is firm enough to withstand the subsequent weaving without "hairing off", "buttoning", "dorning", or breaking, but not so firm as to impair the build of the cloth.

An oversized warp may so impair the actual elasticity of the yarn that it breaks under the tension imposed in either beaming, dressing, or weaving; or if the tensile strength of the yarn is more than adequate, may make a yarn so rigid that the weaver cannot obtain the requisite picks per inch, and the cloth construction is impaired. Undersizing may produce a frictional fluff in weaving that causes breakages at the reed. Over-drying may produce hard, brittle warps that cause trouble in beaming. And so on, *ad infinitum*.

Sizing warps for weaving in a naturally damp mill is a different matter from sizing warps for weaving in a naturally dry mill. Or again, sizing adjustment is usually requested for warps to be woven in automatic looms, as, unlike the non-automatic Lancashire loom, the former operates a wider shed for passage of the larger weft package, and drop wires for the stop motion, which tends to additional tension and abrasion of the yarn. I am aware that this is a point that might be contested by the automatic loom makers, but they will please note that I am careful merely to state that sizing adjustment is "usually requested accordingly".

Occasionally, too, sizing has to accommodate and make presentable yarn which by fortuitous circumstance is known to be inferior to the job in hand, and whilst much can be done, there are limits to this sort of "first aid".

Not all warps are sized; some well built twofold and multifold yarns are woven without size.

Weft yarn in warp form, which is customarily of lower twist and generally weaker than warp yarn, is frequently lightly sized to facilitate the subsequent conversion process to weft pirn; but whereas in warp sizing, if error must be made, it is better to oversize rather than to undersize, in the case of weft in the warp form it is better to undersize rather than to oversize, because an oversized weft yarn would not build into a satisfactory pirn and this would cause trouble in weaving.

The sizing of dyed yarn is almost wholly "pure" sizing, i.e. sizing solely for weaving and not for weighting purposes as such; indeed, many colours would be adversely affected by the ingredients of a "weighted size". One of the aims in the pure

\* *Hairing off* indicates a frictional disruption of the yarn hairs in winding, beaming, or weaving, so that e.g. a cloth with a woven coloured stripe which has "haired off" will show odd coloured fibre hairs extending into the uncoloured or dissimilarly coloured ground to the detriment of the cloth appearance.

*Buttoning* indicates a frictional displacement of yarn fibres by the heads and reed of the loom during weaving, leading to the development of firmly attached button-like bunches of fibre on the ends of yarn, causing yarn breaks and impairing the appearance of the cloth.

*Dorning* indicates a complete frictional displacement of yarn fibres, causing a fibre dust or "dorn" which, when occurring during weaving, for example, adheres to the loom; tends to cause yarn breakages by obstructing the heads and reed, and when of coloured origin impairs the appearance of the cloth when it becomes embedded in the weave; and creates an adverse working atmosphere for the operative.

sizing of coloured yarn is to achieve the desired results with as little dulling or change of shade as possible, although this is usually only of a temporary character. Consequently, well prepared cereal starches, both natural and modified, and also wheat flour are used; and clean proprietary size preparations of vegetable origin also come into the picture.

Now, whereas the crossball and ball warp yarn in closed draft is passed through boiling size liquor in a machine largely similar in principle to the open warp dyeing machine, although special attention is given to the cushioned pressure of the exit squeeze rollers, the warp yarn on the beam in open draft is transferred to a slashing machine, i.e. a beam sizing machine, which incorporates a passage through a short size trough and either hot air or hot cylinder contact drying, whence it passes through a wraith to pattern, direct on to weaver's beam.

Throughout this process, each individual end of yarn retains its individuality. As the dyer's beam is usually limited to a maximum of around 400-600 ends, and whereas several thousand ends may be required on the weaver's beam to make the cloth, a number of dyer's beams—the sett for the job—run through the slashing machine simultaneously, the sheet of ends from each beam being maintained in separate identity until the final wraith, when all the ends are individually laid in the wraith to pattern before passing on to the weaver's beam, which then leaves the slashing machine all ready for the loom.

The sett for the job may consist of as many as a dozen beams, in several colours, and it is sometimes necessary to operate separate size troughs to avoid some degree of colour transfer. Natural grey yarn frequently forms part of the sett for sizing.

So in the case of warp yarn processed on the beam this is the end of the job; but not so in the case of warp yarn processed in the ball or crossball form. In the latter, warps which have been shortened in length or thickened in draft prior to wet processing by reeling or doubling, or by being put together with other warps, must be converted back or split to their original identity, for this multiple arrangement of the original warp particulars is the warp dyer's domestic arrangement and the original identity must be reproduced to enable the warps to be beamed and dry-taped in the case of sized warps, or dressed, beamed, and slasher-sized in the case of unsized warps.

This splitting is a system of undoubling and separating, by means of a peg rail for dividing purposes and usually a felt-covered power-driven roller, round which the warp passes and is drawn along. In the same operation the split warps may be individually coiled or plaited for handling and packing.

And so the ball warp and the crossball warp are made ready for either dressing on to weaver's beam or for back beaming and taping on to weaver's beam respectively, all ready for the loom; and most warp dyers in their comprehensive service referred to earlier include these processes in their repertoire.

I might also mention, by way of reminder, that the lease bands which have been maintained intact throughout the previous processes now come into operation in this conversion of warp to weaver's beam and enable every individual end in the warp to be individually identified and placed according to requirements.

Ball warps, which may have, comparatively, an unlimited number of ends are dressed direct on to weaver's beam, according to pattern, because—

(1) a back beaming frame designed for crossballs, having a limited capacity for about 700 ends, cannot accommodate ball warps, which are invariably composed of many more ends;

(2) as ball warps are comparatively short in length, even if they could be accommodated on a back beaming frame, they would not be an economic proposition to set up on either a dry or a wet tape (i.e. a slashing machine), which are machines intended for a system of long runs, e.g. of the order of 2,000-20,000 yd. running length.

It is characteristic of the Lancashire warp trade that any attempt to describe and to give reasons for the various processes in orderly and systematic fashion is a job for a Philadelphia lawyer, and is bound to cause confusion to those unfamiliar with the trade; in this respect I must point out that manufacturers who have an established plant and personnel for warp dressing do in fact dress crossball warps as well as ball warps.

Ball warp yarn which requires to be sized for weaving is always sized before dressing, of course, as the dressing frame is in fact simply a frame in which the warp or warps are set under tension to wind the sheet of yarn, each end through a reed space, on to the power-driven but slowly moving weaver's beam. A characteristic of dressing is the use of a long narrow brush, which is used by the dresser for brushing or stroking down the sheet of yarn as it stretches out to the weaver's beam in order to separate the individual ends and brush up broken ends for repair. Warp dressing is a job of considerable skill and patience.

Crossball warps, which may be either sized, beamed, and dry-taped, or beamed unsized, and wet-taped (i.e. slasher-sized), are first beamed on to back beam on a frame really not very dissimilar in principle from the dressing frame, each end usually running through a separate dent in the reed on to the back beam (so called because it is subsequently placed in a stand at the back of the taping machine for conversion, with other beams constituting the sett, to the weaver's beam). Normally the speed of back beaming is much greater than that of dressing, owing to the smaller number of ends to be controlled.

Several crossball warps of different shade may be run to preliminary pattern on to one back beam if the total number of ends involved does not exceed the capacity of the frame.

As many as twenty back beams, comprising in total some 11,000 ends as in the case of a double-width gabardine in 2/80 counts warp yarn, may be required to complete cloth requirements, and these are set at varying elevations in the long stand of the dry tape, and the ends from each beam brought

forward in open draft, the open yarn draft from each beam separately, up to the wraith, where the separate drafts unite into one draft according to pattern requirements, and these pass on to the power-driven weaver's beam. A sett of back beams makes a number of weaver's beams.

In the case of wet tapping, which is synonymous with slashing, the machine has been described in connection with the sizing of beam-dyed warps.

Again, this dry or wet tapping is a job of considerable skill.

And now a word about that apparent paradox to which I have previously referred—*weft warps*.

Why should *weft* yarn, which can be supplied by the spinner in cop, and dyed in cop all ready for the loom shuttle, be made in warp form for dyeing and be subsequently converted to *pirn*, i.e. wound back to cop form on a tube all ready for the shuttle? The answer is that in cloths such as *coutils*, *gabardines*, and other cloths of entirely single coloured *weft* construction—known as "*selfs*" or "*solids*"—the continuity of shade which can be given by dyeing in the warp form gives the most satisfactory results. And so *weft warps* of 378 ends per warp to suit the *pirn* winding machine, which has 378 spindles and is commonly used to convert the warp to *pirn*, are a regular portion of the warp dyer's business.

I should mention that, again, the exception that proves the rule is a *pirn* winding machine of 500 ends capacity; and also that, whereas some *weft warps* are wound direct to *pirn*, some are first back-beamed and thence to *pirn* according to circumstances.

And now, having briefly covered a considerable field of operation, we may examine but a few of the cloths whose component yarns pass through the warp dyer's nimble fingers, and some of the specifications and characteristics involved. In a paper which attempts to glance at so many aspects of warp dyeing, the form must of necessity be somewhat superficial and lack detail, and so it is possible only to mention a few of the many fabrics whose coloured production is largely the concern of the warp dyer, but these representative few will indicate something of the variety of the fabrics and of the operative technical considerations. (*Cloth samples were displayed.*)

#### TICKING

This fabric is customarily either a coloured striping or a floral brocade or damask, and of course is designed for making bed mattress covers. Striped ticking is usually used for the flock- and hair-type mattress and the brocade and damask ticking for the more expensive box and pocket spring mattress, not being specifically designed for retaining a flock or hair interior. The better-quality ticking, whether striping or damask, is designed for durability and is very firmly woven. The familiar black and white or blue and white striped ticking is a firmly woven twill, whereas the fancy striped ticking, which is not so strong a fabric, usually features a bold sateen striping to accentuate the colour design. Ticking is calendar-finished and this frequently includes a wax-back finish, all of which in addition to improving the

appearance of the fabric closes the face of the fabric, a desirable feature to prevent the working through of the enclosed mattress filling.

In the main, direct colours are used for ticking, although the black and the blue in the narrow-striped ticking are usually sulphur colourings; basic colours in smaller quantities are also used in the fancy striped ticking. There are no fastness specifications for ticking other than that the colour must not mark off (nor hair off) during weaving, particularly when bleached white is used along with colour, as is frequently the case.

#### HANDKERCHIEF

Despite our austerity the ubiquitous handkerchief may still be either decorative or utilitarian in purpose, and the fabric is usually of a plain weave, although sateen rib effects are frequently introduced. As woven, the cloth width may be designed to yield two gentlemen's handkerchiefs or three or more ladies' or children's handkerchiefs. In the yarn-dyed fabric the colouring effect may be a simple edging, or a wider coloured border design, with either a plain or check centre and maybe a cord effect.

A careful manufacturer whose warp and *weft* colourings are in different hands will ensure that the dyers concerned co-operate in the use of dyes of the same identity, so that after the piece bleach finish the warp and *weft* colourings are alike; the appearance of a handkerchief would be impaired if, for example, in a green motif the *weft* green changed to a bluer tone and the warp green to a yellower tone of green on piece bleaching, or mercerising and bleaching, as the case may be.

The fabric is given a very smooth finish, and with few exceptions only first-class vat and azoic colours of the highest fastness may be used to withstand the finish employed and the subsequent repeated domestic boiling.

#### GINGHAM

This familiar fabric is chiefly of a coloured check character and is used for summer dresses (particularly children's dresses), light overalls, and sundry domestic requirements, the colouring being often of a bright contrasting character—a clean cheery fabric. In the majority of cases it is a plain weave, although there are figured dobby effects. As in the case of handkerchiefs, when the *weft* colouring is not processed by the warp dyer, the careful manufacturer will ensure that the warp dyer and the *weft* dyer co-operate in the use of identical dyes to avoid shade divergencies on finishing. Although the yarn-dyed gingham receives only a calendar finish, the best qualities must withstand repeated domestic and laundry washing, and consequently for the best qualities only vat and azoic colours are used, not necessarily of good fastness to bleaching but of satisfactory fastness to repeated washing and to light. In the lower-quality gingham there may be much variation in colour quality; e.g. pale shades may be in direct colour quality; denser shades sulphur; and full bright shades may be basic, vat, or azoic.



## POPLIN

This nowadays somewhat elusive fabric for shirting, pyjama, and other dress requirements, when wholly derived from yarn-dyed colourings, demands the use of vat and azoic dyes characterised by the highest fastness to piece bleaching and repeated laundry and domestic washing, and not infrequently also to the collar Trubenising process which has created a fashionable demand. Dyeing for this high-quality fabric, perhaps as for no other fabric, tests the experience and ability of the warp dyer to the full, combining as it does yarns as fine as 2/140s counts, colour qualities requiring the most careful technical application, and also the manufacturing practice of maintaining coloured stock warps from which cloth requirements are manipulated. When yarn-dyed the colourings of this characteristic poplin weave are essentially striping effects, with or without a delicately coloured ground effect, and this latter demands that continuity and accuracy of shade to which I have previously referred and which is essential to the desired effect. The Trubenised collar development, which produces a permanently stiff collar by introducing a cellulose acetate fabric between two layers of the coloured poplin fabric and effecting a bond by passage through a solvent for cellulose acetate, e.g. a mixture of trichloroethylene and methyl alcohol, is an additional problem in the dyer's careful selection of dyes, for some dyes otherwise of excellent fastness for poplin requirements are liable to solvent action by the bonding solvent, with consequent bleeding of the colour, and therefore cannot be employed for Trubenising purposes. The azoic dyes, which are most suited to the production of the denser shades, are particularly prone, generally speaking, to this serious disadvantage.

## GABARDINE

Particularly appropriate to our East Lancashire climate, this well known cloth is a characteristic warp-dyeing speciality, for it frequently involves a continuous dyeing run of some 2-2½ miles of high-quality 2/56 or 2/80 counts yarn of 26 t.p.in. (i.e. several more turns per inch than the 15-18 for the same yarns for poplins) in difficult shades of sulphur quality. Usually in the case of the warp yarn proper the shades are of a delicate character and in the case of the weft yarn in warp form of a rich dense character, and the quality standard set, in both the accuracy and the invariability of shade, is most exacting, for this closely woven warp twill fabric reveals in remarkable degree, by weft "barriness" or warp "stripiness", the slightest variations in production. Indeed, so sensitive to production variations is this fabric that even yarn tension variations in beaming, between one warp and another, may eventually show as warpway shadows, particularly so if the beamed warps comprising the tapping sett have not been laid in the wraith of the dry tape end and end, i.e. in strict individual sequence to give the maximum dispersion of ends from each warp across the width of the cloth. A sett of 16 or 20 warps of 2/80s counts for a double-width gabardine of 54 in. may comprise a total of 11,000 ends, which for best results should

be laid individually end and end in the taper's wraith; and this may constitute a dyeing weight of some 1100 lb. of yarn. It is only by warp dyeing that satisfactory results can be obtained for a job of this type, and of course this applies also to the associated weft, which for this very reason is prepared and dyed as warp and then converted to weft pirn after dyeing. Sulphur dyes satisfy all gabardine fastness requirements, which are fastness to water, to light, to wax or similar showerproofing, and to dry cleaning.

## COUTIL

This corsetry fabric, which reveals something of its glamorous purpose by its tonal peaches, roses, apricots, its nudes and fleshies and so called French greys, is counterpart to the gabardine in its exacting standard of production and in its technique of dyeing except, of course, that yarn for coutil, warp and weft, is bleached white before dyeing and is dyed in the most delicate direct-quality shades. Cleanliness is the hallmark of production, for the slightest speck or smudge will mock the unfortunate dyer when the cloth pieces are examined. With high-quality standard self-colour cloths such as the coutil and the gabardine it is essential that all the warps whose total ends constitute the cloth width should be processed simultaneously side by side, and only by warp dyeing can this be achieved.

Vat-dyed coutils are not unknown, but there is so little dye on the yarn that direct-quality dye is adequate for washing fastness, and, of course, fastness to light is *not* required.

## FLANNELETTE

Although the coloured striped flannelette has somewhat passed its fashionable heyday, it still forms an important section of the warp dyer's business and is characterised by the wide range of colour qualities employed—with discretion, not with abandon. There are varying grades of flannelette calling for varying all-round colour fastness, but direct, developed, basic, sulphur, vat, and azoic dyes may be employed together in the one fabric according to colour design requirements. The customary fastness specification is that of domestic washing, and considerable practical experience is required in selecting the colour quality for each colour in a design. The loom-state cloth has rather a prosaic appearance, but the subsequent raising of the cloth face greatly enhances its appearance and attractiveness, and speciality finishes produce very pleasing effects in the handle of the cloth.

## FURNISHING AND CASEMENT

One cannot concisely discriminate between these two fabrics, indeed one can best regard them more as a division of purpose of the same fabric, and it is in this that the greatest opportunity for artistic production and appreciation occurs, whether it be the simple-weave gay striping or the more sombre rich brocade and tapestry of complicated jacquard weave. Colour requirements are mainly fastness to light and the associated resistance to tendering of the fibre under conditions of exposure (particularly for the casement) and good penetration of the

fibre by the dye (particularly in the case of the furnishing), also fastness to washing and dry cleaning according to the nature and purpose of the fabric. Nevertheless, the dyer is called upon to employ dyes whose margin of quality varies considerably with respect to both fastness to light and fastness to washing, and this does not appear to be dictated by considerations of cost, for the colourings of some casements of elaborate and costly construction are not, as one might expect, in appropriate vat quality. Having regard to our capricious climate it may be a reasonable circumstance, but I always feel that a costly fabric of real artistic merit is deserving of the best-quality colourings a dyer can employ.

#### WEST AFRICAN

Under this description we have a variety of styles, and much detail would be required for a comprehensive survey; consequently I have only selected two styles, whose appearance and purpose are rather outstanding. First, the bizarre, brilliant, and ornamented fabric whose design has tribal implications, in which vat and azoic dyes are largely used; and second, the style euphonicly known to the trade as *bleeders*. This term is of technical origin and refers to the particular and characteristic requirement that the colour design on wet treatment shall in part bleed on to the adjacent cloth ground, i.e. warp on to crossing weft, or weft on to crossing warp, producing results of peculiar attraction for the fashionable West African.

This second style is really an imitation of an original native Indian fabric, the Madras headkerchief, used for head coverings, loin cloths, etc.

The original fabric is a somewhat primitive production from hank yarn, the dyeing being done in a shallow earth pit and the yarn woven on crude frames whilst still wet. During the daytime the fabric in the frame dries, but during the night-time it becomes damp again; under these conditions the crudely dyed yarn stains the adjacent fabric, and this cycle continues until the completion of the headkerchief.

The result is characteristic and inimitable (producing a sort of woven-cum-printed effect), and although the commercial copy with which we are concerned is of similar appearance, it cannot be said to be a faithful reproduction of the native art.

In the commercial production the yarn is dyed with a base colour, e.g. sulphur blue or black, direct yellow, azoic red, and then well sized and dried. Then the yarn is passed through a concentrated solution of a basic dye, e.g. Methyl Violet or Methylene Blue in the case of the sulphur blue or black base, Auramine in the case of the direct yellow base, and Magenta or Rhodamine in the case of the azoic red base. The cloth so produced is then finished with the object of bleeding the basic dye on to the adjacent cloth ground. The whole technique is by no means so haphazard as this brief description might imply, for definite preferences are demanded in the degree and the shade of the "bleed".

This fabric is customarily a highly coloured fancy check, and is made principally for the West African market.

(The many sample cloths displayed at the lecture illustrated the two styles.)

The first style is a normally woven and dyed cloth.

#### DENIM AND DUNGAREE

These closely associated fabrics are designed for hard usage as overalls and boiler suits and are invariably firmly woven twills, the warp yarn of which is very firmly sized.

The essential difference between the two fabrics is that, whereas the denim has a coloured warp and a natural weft, or in certain cases a weft of different colour from the warp, the dungaree warp and weft are dyed the same colour to make a self-colour cloth.

Indigo Blue and Cutch Brown are the dyes commonly employed, and sometimes sulphur dyes. The fastness requirements demand a well penetrated yarn the colour of which will withstand an unusual degree of friction without rubbing "bare"; the colour must also withstand severe washing treatment with reasonable results. Most of these cloths are now shrunk-finished by either the Rigmel or the Sanforise processes.

#### REGATTA

This 2/1 twill fabric is essentially an institution cloth, i.e. a cloth used in making uniforms and allied garments for hospitals, homes of various sorts, Government departments, Council establishments, and in fact for any institution which requires hard-wearing, practical-looking, coloured service garments of satisfactory fastness to regular laundry treatment; the colouring is, of course, confined to vat and azoic dyes, including Indigo. The designs are varied: they may be entirely self coloured, single- or multi-coloured stripes, or single- or multi-coloured fancy checks.

The warp yarn is always firmly sized and the loom-state cloth receives only a shrink finish; consequently bleached yarn is used to obtain the many white and colour designs that are in vogue with this fabric.

#### LINING AND PROOFING CLOTHS

This group of fabrics has such extensive use and the fastness specifications comprise so much detail, both precise and conjectural, that one could devote a paper entirely to the subject. Examples of coloured proofing fabrics are—

- (1) Gabardine raincoats and their loose linings
- (2) Light rubberised fabric mackintoshes
- (3) Heavy rubberised, single- and double-texture fabrics for shoe tops, valises, motor-car hoods, and all sorts of heavy waterproof coverings.
- (4) Identification cord, for cable and hose coverings, etc., which also comes within proofing specifications.

These fabrics may be either showerproofed, as in the case of gabardine raincoats and linings, or proofed by rubberising. For convenience one can divide these various fabrics into four classes

according to the type of proofing applied, as follows—

(a) **SHOWERPROOFING**, which may imply a form of wax proofing, or Velan proofing, and which is customarily associated with cotton gabardine rain-coats, both the outer coat fabric and the inner loose lining; and this may be combined with a preliminary acetate of alumina filling treatment to render the fabric non-absorbent to water.

(b) **RUBBERISING OR VULCANISING**—This may be either—

(i) **Cold Liquor Cure**—This is usually associated with the single-texture rubberised mackintoshes in which rubber is applied to one face of the fabric, and in this case the fabric may function as the inner lining of the composite fabric, as in gentlemen's mackintoshes, or the outer face as in ladies' and children's mackintoshes.

(ii) **Dry Heat Cure**—This is usually the procedure for the double-texture fabrics, in which two fabrics are bonded together by a rubber application, which may be preceded by the non-absorbent filling treatment; the heavier type of gentlemen's mackintosh is an example of the fabric that may be so treated.

(iii) **Steam Heat Cure**—This is usually the process for the heaviest double-texture type of water-proof coverings, and again may be preceded by the non-absorbent filling treatment.

These coloured fabrics may be in checked, striped, or self-colour designs and the type of dye used is very varied, direct, sulphur, developed, and occasionally vat and azoic being all concerned in proofing colourings.

The usual specifications are—

- (1) Fastness to light and water
- (2) Freedom from acid and alkali
- (3) Freedom from grease
- (4) Freedom from metallic salts, i.e. those of copper, manganese, chromium, and iron
- (5) Insolubility in cold naphtha solvent and stability under the conditions of vulcanisation, e.g. to sulphur monochloride or to steam heating in an autoclave
- (6) Fastness to a mercerised and schreiner finish.

However, these do vary with circumstances; e.g. fastness to light is not usually required in the case of an inner lining proper.

Although great emphasis is given to freedom from metallic salts, particularly those of copper and manganese, in rubber-proofing, there is considerable divergence of opinion in the matter of permissible limits. Complete freedom from copper is not commercially possible. For example, all cottons contain traces of copper as a natural constituent; contact with copper or brass during processing is inevitable; and it is unlikely that even the dyes specially prepared by the manufacturers for dyeing yarn for subsequent rubber-proofing are completely free from copper. In the absence of any official specification the general practice in this country is to fix the upper limit for copper content at 0.01%. It is well known that copper can cause devastating deterioration of a rubber proofing but does not always do so, and the pros and cons of this

subject of metallic degradation are manifold; indeed, to quote an authority, there are few subjects on which there is so complete absence of agreement. The chemistry of this metallic degradation is somewhat obscure, and it is suggested that the process may be connected with the form in which the metal is combined, or may be combined, during the vulcanising process; this probably explains why one fabric containing only a trace of copper or manganese is virtually destroyed and another containing considerably more is satisfactory.

The dyer must be experienced in the pitfalls and the responsibilities involved, and orders for proofing colours must be carefully vetted in the knowledge that the specification on a commission received is something which very probably has been passed, in print of increasing boldness, from distributor to merchant, merchant to manufacturer, and manufacturer to dyer, much in the manner of a very "hot brick"—and not infrequently a very doubtful foundation stone for the dyer.

Now, if I may leave the descriptive for a more tendentious aspect of warp dyeing, I should like to fulfil my original invitation, which included a suggestion to give expression to any personal opinion on any relevant matter on which I had pronounced views, and wisely or unwisely, I am moved to disclose two thoughts—

First, it will I think be generally agreed that wherever colour fastness is desired, the tendency throughout the trade is for faster colourings, and I think this is a<sup>4</sup> the instance of both the producer and consumer—and properly so. Consequently the employment of tests to achieve a recognised standard of fastness is becoming more and more evident—and again properly so. But whereas the form of any suitable standard test is a matter of precision and careful qualification by the technologist, the trade interpretation of the test results is usually less well defined and impatient of any qualifying points that may demand a careful interpretation of the results. The consumer of dyed yarn, whether manufacturer, merchant, or the purchaser of the ultimate article, views the result of a fastness test in the manner of the judge who wisely prescribed that by any verdict or sentence, justice must not only be done, but must seem to be done; and by this interpretation consumers are very sceptical of a washing test which purports to prove adequate colour fastness and at the same time displays a degree of staining by the colour.

This preamble converges on the employment of the Society's No. 2 washing test.

As everyone will know, this washing test is one of several designed to determine the suitability of any dyed shade for subsequent varied usage. It is, of course, a treatment of the dyed yarn (preferably plaited with grey and bleached yarn) in a 0.2% solution of soap at 140°F. for 1½ hr., and this test has become embodied in trade specifications, notably the Utility cloth specifications. With the greatest deference I want to submit that in certain circumstances the employment of this test is something of an anomaly, is rather misleading, and the



interpretation of its results an unfortunate cause of suspicion.

By way of explanation I want to make two points. First, the original test details carry an important qualification—

A coloured material is deemed to have passed the test to which it has been subjected, if the loss of colour is not greater than that of the standard, and to have failed the test if the loss of colour is greater than the standard. The permissible degree of bleeding must be subject to individual requirements.

and this is, of course, clear and reasonable to the technologist. But what of the two fundamentals—the "standard" and the "individual requirements"? Are the Utility shades sufficiently well defined standards to function as precise fastness standards?

And what of the individual requirements governing the permissible degree of bleeding?

Obviously, the individual requirements must be varied, and as they are merely noted but not defined, the only individual requirement to which reference can be made is the experience of well established trade practice. Now in the case of the coloured flannelette the trade has made use of all qualities of colour, correctly assessing and employing dyestuff qualities according to fastness limitations and washing practice. The Utility flannelette shades, for example, are designed on this basis of past experience, but the association of the No. 2 washing test with these shades causes confusion by reason of some of the test results, which reveal a degree of bleeding or staining that causes the consumer a concern which is not relieved by pointing out that the result is that which one normally expects under the conditions of the No. 2 test; and here my second point emerges. Is the No. 2 washing test a suitable test for the Utility flannelette and similar cloth ranges? Again, reference to the original test details covering tests No. 1-4 discloses that No. 1 test is defined as corresponding to the fastness requirements of a home wash; No. 3 and 4 to severe laundry boils; but No. 2 is rather vaguely relegated to the unspecified and doubtful patronage of "an intermediate class".

In searching for independent support for my feeling that the No. 2 test is misapplied (please note I say misapplied not misconceived), I find in the British Laundries Research Association's authoritative publication *Technology of Washing* that in modern laundry technique the temperature of any of the several wash liquors applied to coloured goods is below 140°F. and the duration of each individual wash not more than 15 min. That is, the cumulative "bleeding" and staining by long immersion in one liquor (as in the case of No. 2 test) are avoided.

I also find in Williams' *Textiles on Test*, a critical reference work compiled with the object of enlightening and safeguarding the consumer, the following comforting sentence—"sensible people usually wash coloured fabrics under the mildest possible conditions".

I am aware that the Society's Fastness Committee has published a revision of the original fastness tests, but I cannot foresee that the results from the application of the revised No. 2 washing

test will be any less likely the cause of trade misunderstanding than the results from the original test.

In commercial practice more trouble and suspicion arise from the staining of the ground fabric than from loss of colour density or change in shade, but the scheduled interpretation of the revised No. 2 test results still leaves the staining factor to discrimination according to governing circumstances. This is understandable, of course, to the experienced technologist, but I submit that a test productive of a result which requires qualified interpretation should not be lifted out of its context, as it were, and widely superimposed, as it has been, as a simple visual test of washing fastness. I would emphasise that this situation is not due to any defect inherent in the test itself but to its casual use and interpretation by the trade.

My second thought is perhaps somewhat unusual in a paper before this Society, but I feel it is a matter of essential practical concern to the dyeing trade as a whole and to the technologists of the trade individually.

This Society is concerned with perpetuating technical progress, and anyone knowing the Society must feel confident that adequate scientific progress and application are thereby assured. But it does seem to me that, whereas our science grows richer and our scientists increase, our craftsmanship grows poorer and our craftsmen decrease.

The knowledge and practice of dyeing extend as far back as historical record and conjecture permit, and the dyeing trade must be one of the oldest trades of mankind: it was born in craft and largely maintained and nurtured by craftsmen throughout the ages—but what of the trend of events nowadays? Can we look in the future and be content that our craftsmanship also will grow richer and our craftsmen increase, as they must, for whereas the scientist seeks the best in new experience and strives to establish it, the true craftsman by circumstance remembers the best in past experience and strives to perpetuate it, and the two are complementary and essential to balance?

I feel that true craftsmanship is in danger of diminishing and that the dyeing trade will be very much poorer if it remains nonchalant about it.

The disruptive effect of two world wars in half a lifetime, the development of so called clean and light industries, the social changes, the labour shortage, and the experience of the mass diversion of labour at the whim of State policy are contributory factors and endanger the proper continuity of, and pride in, craftsmanship.

I venture no solution of the problem, but I feel it should be constantly in the minds of all responsible technologists in the trade, and I suggest it is surely an anomaly that in a craft as old as the hills, or should I qualify that and say as old as the Pennines, for I confine my remarks to East Lancashire, there should be no deep rooted and recognised form of apprenticeship for the labour on which this trade depends.



There is much very commendable planning of incentive to production, but should we not also plan to strengthen and to perpetuate that all-important craftsmanship?

In the old days economic circumstance was an incentive to craftsmanship: I doubt whether any practical person would hold that true to-day.

Ought we to do something about it?

The author gratefully acknowledges assistance from colleagues and customers, and the permission of Messrs. The British Cotton and Wool Dyers' Association Ltd. to publish this paper.

### Discussion

Mr. F. PARROTT: Does Mr. Marr think that the presence of copper in its non-ionised state would be detrimental in dyed warps subsequently to be rubberproofed? Dyers apparently use cotton dyes for this trade with success, without knowing that many of them are copper complexes. Although it is fairly obvious that the total copper content of yarns dyed with this class of dye will be very much higher than the permitted amount, yarns so dyed have, in fact, proved perfectly satisfactory for rubberproofing.

Mr. MARR: I am in general agreement with the speaker. The presence of copper in a dyed yarn for rubberproofing can produce a disastrous result but does not always do so; insufficient is known about the matter to give a precise explanation. It is

believed that the circumstances are dependent on the form in which the copper is combined, or may become combined, during or after processing, "free" copper being a potential danger. The dyer advisedly continues to use those dyes which have been found to give a satisfactory result for a customer's particular proof finish; and proofing finishes are not all alike in their potential degradation by metals.

Mr. S. BURGESS: In the dyeing of cotton warps for cloths to be rubberproofed, is any wet fastness required, either processing or consumer fastness?

Mr. MARR: Fastness to water does appear in the numerous specifications, not as a processing requisite but as a consumer requisite, when e.g. a coloured lining fabric appears as the outer face of a rubberised fabric, as in the case of ladies' and children's coloured striped and checked mackintoshes. (*He illustrated the point by reference to proofing fabrics displayed.*)

Mr. H. WAKEFIELD: What is the minimum number of ends for dyeing?

Mr. MARR: A likely number of ends in a warp draft would be of the order expressed by "counts  $\times 80$ ".

Mr. H. W. BEST-GORDON: What type of yarns are basic dyes used on, and what purpose are the yarns intended for?

Mr. MARR: Among other uses, basic dyes are regularly used in warp dyeing yarn for ticking and flannelette.

## MIDLANDS SECTION

Meeting held at Carpet Trades Ltd. Canteen, Kidderminster, on 27th January 1949,

Mr. G. RAINSFORD in the chair

(joint meeting with the Kidderminster Branch of the Textile Institute)

### The Dyeing of Direct Cotton Dyes on Fibro Carpet Yarns in Hard Water

M. V. CAMPBELL

The range of direct cotton dyes available for use in hard water is considerably restricted by the following factors—(a) many direct dyes are insoluble in or precipitated by such water at the boil, and irrespective of the sodium chloride concentration give little or no dyeing; and (b) others are so sensitive to the large amounts of electrolytes present that in the absence of added sodium chloride they give a heavy "strike".

Many of the Class B (S.D.C. classification) dyes become Class C dyes when used in hard water, but they can be restored to Class B by the addition to the dyebath of small amounts of Calgon T.

Chlorantine Fast Brown BRLL represents a reference type for the dyes in (a) which are redissolved by additions of Calgon T to the dyebath; while Chlorantine Fast Blue GLL 200 is a reference type for the dyes (b), in the dyeing of which an addition of 0.5 g. of Calgon T per litre acts as a restraining influence and reduces the "strike".

Waters of 5° English hardness or more respond to the restraining influence exerted by Calgon T.

Other similar agents and their properties in dyeing direct dyes in hard water are discussed.

### Introduction

The objects of this paper are (a) to illustrate the difficulties which may be encountered in the dyeing of direct cotton dyes in hard water, and (b) as a result of experimental work which has been carried out, supported by bulk dyeings based on these experiments, to offer suggestions for overcoming these difficulties.

Although the paper refers in particular to Fibro (Courtaulds) carpet yarns, and the dyeings have been carried out in water of a certain hardness, the

results are applicable to other types of cellulosic fibres and varying types of hard water.

### COMPARISON BETWEEN ACID WOOL DYEING AND DIRECT COTTON DYEING

For the benefit of those who are not familiar with the methods of dyeing cellulose with direct cotton dyes, it may be of interest to make a comparison with the dyeing of wool with acid dyes, a process more familiar to the carpet industry. In the dyeing of wool with easy-levelling acid dyes,

the components of the system are (a) wool fibre, (b) water, (c) dye, (d) Glauber's salt, and (e) acid. The acid is added to the system to assist the combination of the dye with the wool, and with the type of acid dyes in use in the carpet industry the absence of acid means that little colouring matter is absorbed by the wool, which is not dyed.

In the dyeing of direct cotton dyes on cellulose, the components of the system are (a) cellulose, (b) water, (c) dye, and (d) common salt, Glauber's salt, or other electrolyte. The addition of (d) to the system causes the dye particles to aggregate or increase in size, and it is assumed that dyeing takes place by the trapping of the dye molecules within the canals or pores of the fibre. Generally speaking, the absence of any electrolyte in the system means that no dyeing of the fibre will take place. There are exceptions to this, and it has been pointed out by Boulton and Morton<sup>1</sup> that Benzopurpurin 4B (C.I. 448) is absorbed by cellulose in a system very carefully freed from all electrolytes. Other dyes have varying affinities for cellulose in the absence of added salt.

#### ELECTROLYTES AND THEIR ACTION IN DYEING CELLULOSE

These have been discussed at length by various authors<sup>2-7</sup>, and it is interesting to refer to a paper by Boulton<sup>5</sup> in which he mentions the initial absorption of the dye by the surface molecules of the fibre—

This the dyer calls the "strike" and it determines in part the rate at which the dye-bath is exhausted and the degree to which exhaustion can be kept under control by the dyer, whose job it is not merely to exhaust the bath but to distribute the molecules uniformly throughout the material he is dyeing. The degree to which this deposition of an "outer skin" of dye takes place is determined by the presence of salt in the dye-bath, and the sensitivity of the dye to the salt present.

Boulton also points out that the levelling of a bad "strike" depends upon the diffusion rate of the dye being used, and this in turn determines the time required for a dyeing to attain uniformity, and may vary between half an hour and twenty-four hours.

#### PERFECT CONDITIONS

In the dyeing of Fibro for cut-pile fabrics, the dyer is faced with not only the problem of obtaining perfect uniformity throughout the batch of the material he is dyeing, but also that of complete and perfect penetration of the individual fibres. The "strike" is therefore of particular importance. If we could choose for ourselves the perfect conditions of (a) pure cellulose, (b) pure dyes, and (c) pure water, free from electrolytes, then the control over the rate of exhaustion of direct dyes would be a simple matter of regulated additions of salt to the dyebath. Fibro is a relatively pure form of cellulose, and that which is being received into the carpet industry for pile yarn is clean and free from impurities.

Dyes in the direct range can be obtained in a highly concentrated form, and relatively free from salt. Unfortunately, the dyer is not always in a position to choose his water supply, and that which is available to many of us in the Kidderminster

area—particularly the deep well water—contains fairly high amounts of dissolved solids in the form of calcium and/or magnesium hardness. There is one supply known to have a total hardness of over 40° English hardness, or more than 500 p.p.m. as  $\text{CaCO}_3$ , and waters of 18–25° are common.

Electrolytes of this nature in any appreciable quantity are sufficient to cause a very heavy "strike", giving rise to rapid exhaustion of the dyebath with the consequent risk of initial unlevelness, which may or may not be corrected, depending upon the class of dye employed.

#### RAPID EXHAUSTION CAUSED BY CALCIUM AND MAGNESIUM SALTS

To illustrate the rapid exhaustion caused by calcium and magnesium salts, a series of dyeings has been prepared with Chlorantine Fast Blue GLL 200% in distilled water, with additions of 0.0, 2.5, 5.0, 10.0, and 20.0% of the following salts—

Sodium chloride	Ammonium oxalate
Sodium sulphate	Calcium chloride
Sodium acetate	Magnesium chloride
Ammonium acetate	Barium chloride

The dyeings carried out without additions are undyed. In the case of common salt and other sodium salts the aggregation or "salting on" is gradual and increases progressively with the amount of salt added, but in the case of calcium and magnesium chlorides the depth of shade obtained with only 2.5% addition is almost equal to that obtained with 10% of the sodium salts. This is attributed to the increased "salting on" power of the bivalent calcium and magnesium ions compared with the univalent sodium ion.

#### T.B.W. HARD WATER AND ITS EFFECT ON DIRECT DYES

The water available at T. Bond Worth & Sons Ltd., Stourport-on-Severn, and which is used for dyeing purposes, is obtained from a well 300 ft. deep, and contains hardness totalling 296 parts per million, made up as follows—

Temporary hardness due to lime	...	180 p.p.m. as $\text{CaCO}_3$
Permanent hardness due to lime	...	3 p.p.m. as $\text{CaCO}_3$
Permanent hardness due to magnesium	...	113 p.p.m. as $\text{CaCO}_3$

(Where this water is used for subsequent experiments it is referred to as T.B.W. hard water.)

A dyeing carried out in this water with Chlorantine Fast Brown BRLL 200% was a complete failure due to precipitation of the dye.

Laboratory tests revealed that a great many of the faster-to-light direct dyes could not be applied to cellulose in T.B.W. hard water because of either (a) their insolubility in or precipitation by that water, or (b) the heavy "strike" obtained due to the large amount of electrolytes present. Those dyes which could be grouped under (a) gave little or no dyeing on Fibro, irrespective of the presence of added sodium chloride, while those under (b) gave a heavy "strike" even in the absence of sodium chloride. Of twenty-nine dyes tested only eleven were completely soluble in this water.

It will be appreciated that some difficulties present themselves when we attempt to apply direct dyes in this type of hard water, due to the

presence of large quantities of calcium and magnesium, and if satisfactory results are to be obtained some method must be found to neutralise the effect of these salts.

These difficulties can, of course, be overcome by (a) a demineralising process, or (b) a softening process, neither of which was available at T. B. Worth & Sons Ltd.

The former is a complete answer, since by the methods available it is possible to obtain water completely free from electrolytes.

Softening processes offer a partial solution to the problem, much depending on the type of water and the method of softening adopted. The Permutit base-exchange process will give a water capable of dissolving the dyes, and although the strike is reduced by the presence of sodium salts instead of calcium or magnesium, the amount of total dissolved solids is still high, and complete control over the strike is not obtained. The alkalinity developed by some softened water on boiling is often objectionable when dyeing with direct cotton dyes.

In the course of the original experiments to try and obtain well penetrated and commercially level dyeing under these adverse conditions the use of Calgon T appeared to offer a solution.

#### THE USE OF CALGON T

Calgon T, manufactured by Messrs. Albright & Wilson Ltd., is a glass-like substance containing about 67.5%  $P_2O_5$ , and is often referred to as *sodium hexametaphosphate*. It has the power to sequester or "lock up" the calcium and magnesium salts found in water into a soluble complex.

Dyes which were insoluble in T.B.W. hard water were found to redissolve when Calgon T was added to the water in very small amounts. Calgon T, therefore, appeared to supply a solution to part of the problem, but being an electrolyte, it was thought possible that its addition to a dyebath already containing 290 p.p.m. dissolved solids might tend to increase the strike of the dye and thus accentuate the second difficulty.

The extent to which this occurred was ascertained in the following investigation.

#### Experimental

It was intended that this investigation should follow practical lines as far as possible, so that any findings could be easily related to large-scale practice. At the same time it was thought desirable to follow in some degree the procedure adopted by other workers who have carried out investigation into the dyeing of direct cotton dyes, mainly in distilled water.

#### PROCEDURE

**YARN**—A supply of yarn was obtained from Messrs. Jute Industries Ltd., spun from a selected batch of 18-denier 8-in. matt Fibro to 2/12 jute-count carpet yarn. No lubricant was used during the spinning.

**SCOURING**—The yarn contained a small percentage of residual soap, which remained in the Fibro staple after washing, but as in normal practice such yarn would be dyed without a preliminary

scour, it was decided to carry out the first trials without any pretreatment. At a later stage the investigation could be extended to cover condenser-spun yarns, which would have to be scoured before dyeing.

**WEIGHT OF HANK**—Five-gram hanks were prepared by measuring off 7-yd. lengths of yarn and correcting each to weigh 5 g.

**RESIDUAL ELECTROLYTES**—In an investigation of this description it was desirable that the yarn should be free from electrolytes which might affect the results, and to ascertain this the following tests were applied.

Nine 5-g. hanks were prepared for dyeing as follows—

- Three were boiled in two lots of distilled water for 30 min. and dried.
- Three were boiled in two lots of distilled water for 30 min. and allowed to remain wet.
- Three were untreated.

Dyeings were made with 0.5% Chlorantine Fast Blue GLL 200% (CAC) (chosen on account of its low affinity in the absence of electrolytes), boiled for 30 min. in 30 vol. of the following types of water without further additions—

- Distilled water
- T.B.W. hard water
- T.B.W. hard water containing 2 g. Calgon T per litre.

One of each of the three prepared hanks was used for each type of water, a total of nine dyeings.

The shades obtained in each of the three types of water were almost identical, practically no dyeing taking place in distilled water. It was thus established that the yarn in the unscoured state was sufficiently free from electrolytes for these experiments.

**LIQUOR RATIO**—Following previous workers a liquor : goods ratio of 30 : 1 was chosen, and the dyeings were carried out in 300-ml. glass beakers heated on a hot plate.

**DYEING TIME**—Again following previous example, 30 min. at the boil was chosen, and preliminary trials established that to give a net volume of 150 ml. after 30 min. at the boil it was necessary to commence the dyeing in a volume of 210 ml., the excess 60 ml. being made up with distilled water. Where the net volume at the end of a dyeing differed by  $\pm 5$  ml. those dyeings were repeated.

**STOCK SOLUTIONS**—All stock solutions were made up in distilled water, so that the excess of 60 ml. required at the commencement of the dyeing could be partly made up by the additions of dye, salt, etc. required for the dyeing.

**Dye**—2.0 g. per litre. Where the concentration of the dye differed from the standard 100% allowance was made when making the stock solution, so that in every case 25 ml. of stock represented a 1% dyeing of standard type on a 5-g. hank.

All dyeings made throughout this investigation are 1% standard type or its equivalent.

**Common Salt**—5% solution. 20 ml. represents 20% common salt on a 5-g. hank.



*Calgon T or Other Additions*—10% solution. 3 ml. stock in 150 ml. dye liquor represents a concentration of 2 g./litre.

THE SOLUBILITY OF DIRECT COTTON DYES IN  
T.B.W. HARD WATER WITH AND WITHOUT  
ADDITIONS OF CALGON T

Before proceeding with the experimental dyeings, tests were made to ascertain the solubility of a range of dyes in T.B.W. hard water, with and without additions of Calgon T.

Concentrated stock solutions of the various dyes under test were made up in distilled water and were such that 1 ml. added to the requisite volume of dyebath solution represented a bath capable of yielding a 1% dyeing of standard strength in 30 volumes.

Dyebath solutions were prepared with (a) distilled water; (b) T.B.W. hard water; and (c) T.B.W. hard water with additions of Calgon T to give concentrations of 0.1, 0.2, 0.3, 1.0 g. per litre. 1 ml. stock dye solution was added to each of twelve test-tubes, and made up to 20 ml. with the requisite prepared dyebath solution.

TABLE I  
The Solubility of some Direct Dyes in T.B.W. Hard Water  
with and without Additions of Calgon T  
(s = soluble; i = insoluble)

Dye	Maker	T.B.W. Hard Water	Calgon Value (g./litre)	(a)	(b)
CLASS A					
Chlorazol Blue G	ICI	s	—	—	—
Chlorantine Fast Red K	CAC	s	—	—	—
Chlorantine Fast Yellow SL	CAC	s	—	—	—
Rigan Sky Blue G 400	CAC	s	—	—	—
Solar Blue 4G	S	i	0.4	0.7	—
Durazol Blue 4R 200	ICI	i	0.4	1.4	—
Direct Pink EG 400	Gy	i	0.6	—	—
Rosanthere R	CAC	i	0.6	—	—
Chrysophenine G	LBH	i	0.6	—	—
Chlorazol Yellow 6GS	ICI	i	0.7	—	—
Direct Fast Black B	CAC	i	0.8	—	—
Chlorantine Fast Orange GN 200	CAC	i	1.0	—	—
Chlorantine Fast Orange G 150	CAC	i	1.1	—	—
CLASS B					
Chlorazol Blue B 500	ICI	s	—	1.0	—
Chlorantine Fast Rubine RNL 200	CAC	s	—	—	—
Solophenyl Blue Green BL 250	Gy	s	—	—	—
Direct Fast Orange WS	CAC	s	—	—	—
Chloramine Copper Blue 4G	S	s	—	—	—
Chlorantine Fast Blue 4GL 200	CAC	s	—	—	—
Chlorazol Sky Blue GS	ICI	s	—	—	—
Durazol Orange 2G 125	ICI	i	0.1	—	—
Solar Orange EGL	S	i	0.2	—	—
Durazol Red 6BS	ICI	i	0.2	0.7	—
Durazol Orange Brown 2RS	ICI	i	0.3	0.6	—
Direct Green 2G	CAC	i	0.4	—	—
Chlorantine Fast Green 5GLL	CAC	i	0.5	0.7	—
Chlorantine Fast Blue GLL 200	CAC	i	0.5	0.8	—
Durazol Rubine B 150	ICI	i	0.5	0.8	—
Paramine Fast Brown RL	LBH	i	0.5	0.8	—
Direct Blue BT	CAC	i	0.6	—	—
Chlorazol Dark Blue BS	ICI	i	0.6	1.0	—
Diphenyl Violet BV	Gy	i	0.6	1.0	—
Chlorazol Fast Scarlet 8B 125	ICI	i	0.8	—	—
Stilbene Yellow 2G 160	CAC	i	0.8	1.0	—
Paramine Fast Red F	LBH	i	0.9	—	—
Durazol Grey VG 150	ICI	i	1.3	0.5	—
CLASS C					
Direct Fast Scarlet SE	CAC	s	—	—	—
Chlorazol Brown LF 150	ICI	s	—	—	—
Direct Sky Blue GS	CAC	s	—	—	—
Carbide Black E & D	CAC	s	—	—	—
Solophenyl Yellow FFL	Gy	i	0.4	—	—
Chlorantine Fast Brown BRLL	CAC	i	0.5	—	—
Direct Fast Orange SE	CAC	i	0.5	0.7	—
Chlorazol Brown MS	ICI	i	0.6	—	—
Solophenyl Olive BL	Gy	i	0.6	—	—

The solubility of each dye was first noted in the cold; and here it was observed that where a dye is previously dissolved in distilled water, its solubility in cold hard water is in some cases better than if the dry dye is added directly to the hard water. The tubes were then boiled for 10 min., some dyes being precipitated, while others went out of solution on cooling. The concentration of Calgon T required to maintain complete solubility was noted, and where the tone of the solution in hard water differed from that in distilled water, two figures are given (Table I)—

(a) The minimum concentration of Calgon T in grams per litre required to maintain complete solubility of the dye at the boil and on cooling.

(b) Where there is a change of tone, the figure given is the concentration required to restore the tone of the bath to that given in distilled water.

The Calgon values as shown under (a) bring out an interesting example of yet another way in which direct dyes exhibit their individualistic behaviour. There is a critical hardness at which precipitation occurs for each individual dye; e.g. Durazol Orange 2G 125 (Class B) is insoluble in T.B.W. hard water, but can be brought into solution by the addition of 0.1 g. Calgon T per litre, which reduces the hardness from 296 p.p.m. to, say, 282 p.p.m.

The figures shown are therefore an indication of the solubility of these dyes. But, as well water is liable to rapid changes in composition, so may a dye be rendered insoluble or *vice versa*. It is therefore advisable to ascertain the minimum concentration of Calgon T required to satisfy the condition of the dyehouse water at the time of use.

PRELIMINARY DYEING TRIALS

Preliminary trials were first carried out to ascertain the effect of Calgon T in the dyebath, and in order to formulate broad outlines for the further and more detailed investigation.

Durazol Red 6BS (Class B), although not completely soluble in T.B.W. hard water, was being used for bulk dyeings without the addition of Calgon T with some fairly good results, and it was decided to use this dye for the first tests.

Six dyebaths were prepared containing 0, 0.2, 0.4, 0.6, 0.8, and 1.0 g. of Calgon T per litre of T.B.W. hard water, together with 1% dye on 5-g. hanks of Fibro yarn. The dyebaths were raised to the boil, and a dry hank was entered into each and boiled for 30 min.

The first three dyebaths were cloudy with a scum forming on the surface, while the last three were clear and bright. This was expected, but, contrary to expectation, instead of increasing the depth of shade, the addition of Calgon T appeared to have a slight restraining influence, and even with an addition of 1.0 g./litre the dyeings were lighter than those obtained in T.B.W. hard water without additions.

A further series of dyeings was then made under similar conditions with the salt-sensitive Class C Cotton Red 4B (Benzopurpurine 4B). Four 1% dyeings were made in—

- Distilled water
- T.B.W. hard water

- (c) T.B.W. hard water containing 0.5 g. Calgon  
T per litre
- (d) T.B.W. hard water containing 1.0 g. Calgon  
T per litre.

(a) shows the affinity of this dye for cellulose in the absence of added salt, giving a medium exhaustion; (b) is a fully exhausted shade badly penetrated; while (c) and (d) are both very slightly lighter than (b) but not as light as (a).

As a further preliminary test the effect of time of dyeing was studied, for which the Class B Chlorantine Fast Blue 4GL 200% was chosen. As this is soluble in T.B.W. hard water, highly concentrated, and relatively free from salt, the influence of standardising diluent would be largely obviated.

0.5% dyeings were made in 30 vol. for 2, 10, and 20 min. at the boil in the following waters—

- (a) Distilled water
- (b) Distilled water containing 0.5 Calgon T per litre
- (c) T.B.W. hard water
- (d) T.B.W. hard water containing 0.5 g. Calgon T per litre.

When dyed in distilled water (*a*) and washed off in distilled water, no appreciable dyeing takes place with this dye. In (*b*) the addition of Calgon T effects a very slight "salting on" of the dye, which does not increase very much between 2 and 20 min. The dyeings in T.B.W. hard water (*c*) show a progressive increase in depth of shade as dyeing is prolonged. Those in T.B.W. hard water containing Calgon T (*d*) show little increase in depth with time and illustrate that the restraining influence of Calgon T does not deteriorate.

In previous experiments no particular attention had been paid to the type of water used for rinsing dyeings, but in this series it was noticed that a dye having little affinity in the absence of electrolytes, if dyed in distilled water and washed off in hard water, gave patchy results, due to the rapid aggregation of loosely held dye by the calcium and magnesium salts in the water. In order to obtain consistent results in experimental work of this nature, it is recommended that distilled water should be used for rinsing all dyeings.

### S.D.C. CLASSIFICATION OF DIRECT COTTON DYES

In view of the large amount of work which has already been carried out on the dyeing of direct dyes, mainly in distilled water or water of very low hardness, it was decided that this present work should follow some established principles.

Direct dyes have been divided into three classes, firstly by C. M. Whittaker, and more recently by the Society's Direct Cotton Dyes Committee<sup>8</sup>. Tests have been devised by which direct dyes, when dyed on cotton, can be classified according to their behaviour under certain conditions. The tests used are (a) the migration or levelling test, and (b) the salt controllability test. The dyeings carried out in this work under these two headings are based on the methods recommended by this Committee.

### EXPERIMENTAL DYEINGS

Some thirty separate dyes, including the reference standards chosen by the Direct Cotton Dyes Committee, have been tested, and the dyeings indicated below made with each dye. Dyeings made with a few well known dyes are illustrated in the coloured plates (Fig. 1 and 2), a key to the additions made to the dye bath being given below.

**Key to Dyeings in Fig. 1 and 2\***

(other than those showing effects of waters of lower hardness, refluxing, and mixtures of dyes)

All dyes are the equivalent of 1% standard brands on 5-g. hanks dyed for 30 min. at the boil in the appropriate water containing additions of sodium chloride and/or Calgon T. An excess of 60 ml. distilled water is added to each dyeing to compensate for evaporation, and the boiling controlled to give a net volume of 150 ml. at the end of the dyeing time.

Distilled Water	T.B.W. Hard Water	T.B.W. Hard Water + Calgon T	T.B.W. Hard Water + Calgon T
DYEINGS WITHOUT ADDITIONS OF SALT		Calgon T, 2 g./litre	—

### S.D.C. MIGRATION TESTS

<i>Dyed Samples</i>	20% NaCl	20% NaCl	20% NaCl Calgon T, 1 g./litre	—
<i>Migration Test</i> (2.5 g. dyed sample with 2.5 g. undyed yarn)	10% NaCl	10% NaCl	10% NaCl Calgon T, 1 g./litre	—

### S.D.C. SALT CONTROLLABILITY TESTS

First Dyeings of the Pairs			
0.6% NaCl	0.6% NaCl	0.6% NaCl Calgon T, 1 g./litre	Calgon T, 0.6 g./litre
0.8% NaCl	0.8% NaCl	0.8% NaCl Calgon T, 1 g./litre	Calgon T, 0.8 g./litre
1.0% NaCl	1.0% NaCl	1.0% NaCl Calgon T, 1 g./litre	Calgon T, 1 g./litre

### Second Dyeings of the Pairs

20% NaCl added to the unexhausted dyebath from the first dyeings

\* Chlorazol Blue G 150 is now a Class A dye

DYEINGS MADE WITHOUT ADDITIONS OF SALT—Dyeings were made in 30 vol. for 30 min. at the boil without additions, in the following types of water—

- (a) Distilled water
- (b) T.B.W. hard water
- (c) T.B.W. hard water containing 2 g. Calgon T. per litre†.

(a) The first of this series, dyed in distilled water, shows the affinity of the dye for the fibre in the absence of electrolytes other than that contained in the dyestuff itself. Highly concentrated dyes such as—

Chlorantone	Fast Blue	GLL	200%	...	Maker	Class	Fig.
Chlorantone	Fast Blue	GLL	200%	...	CAC	B	2
Solophenyl	Blue Green	BL	250%	...	Gy	B	1
Chlorantone	Fast Rubine	RNLL	200%	...	CAC	B	—
Durazol	Blue 4R	200%	...	...	ICI	A	1
Chlorazol	Blue B	500%	...	...	ICI	B	—

show practically no dyeing. In others, the natural affinity or the effect of standardising diluent is shown by darker dyeings. The effect of such diluent is shown in another series of dyeings made with (i) purified salt-free dyes, and (ii) standard products containing up to four times their weight in common salt, where in every case the standard dyes give darker shades.

† 2 g. per litre is the concentration of Calgon T required to sequester all the calcium and magnesium present in T.B.W. hard water.

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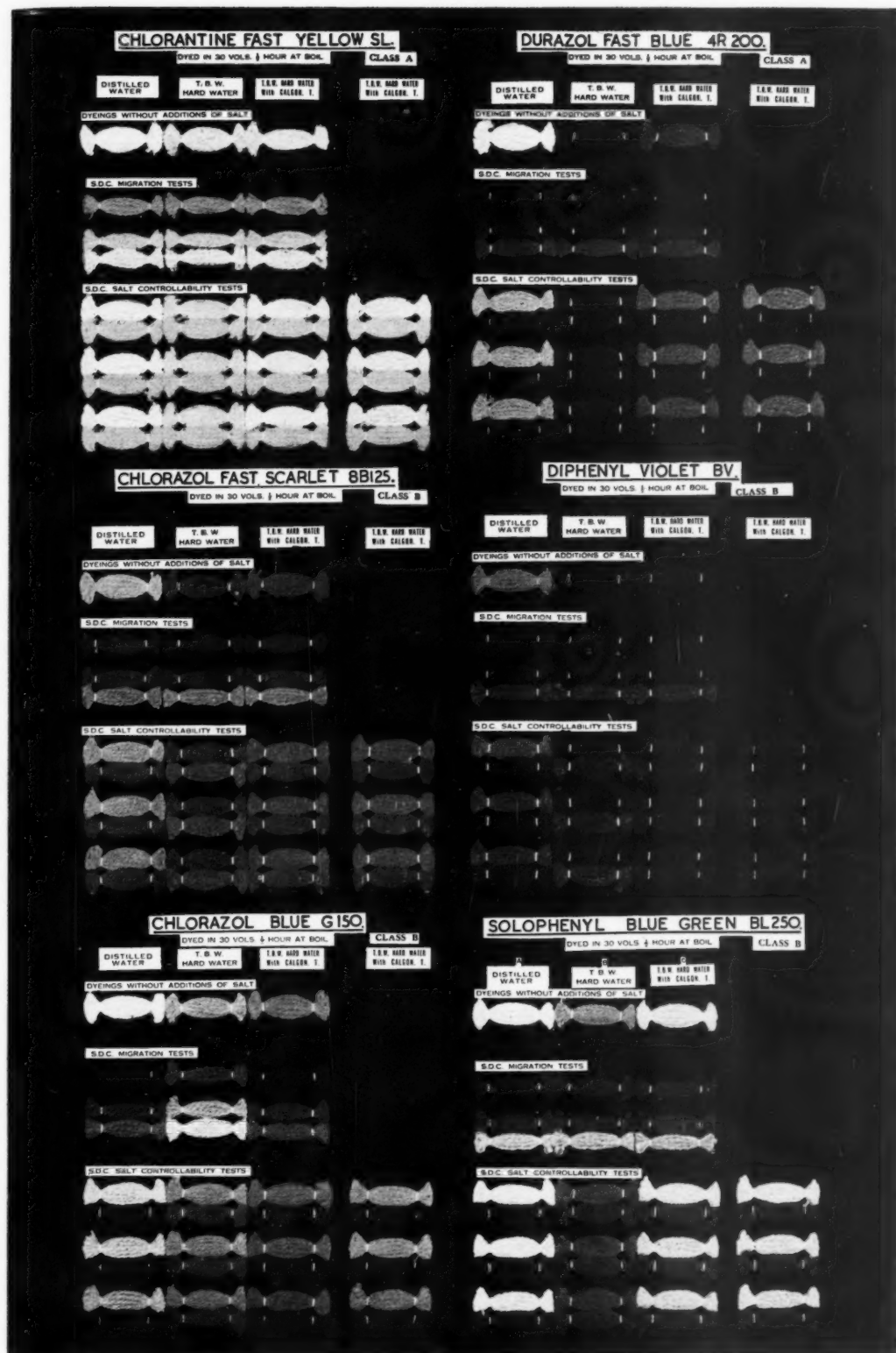
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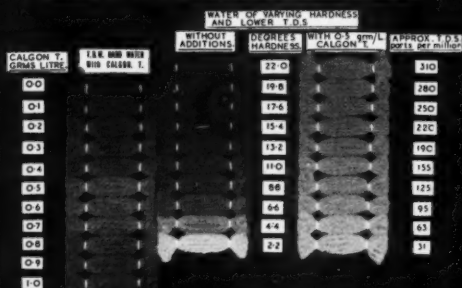
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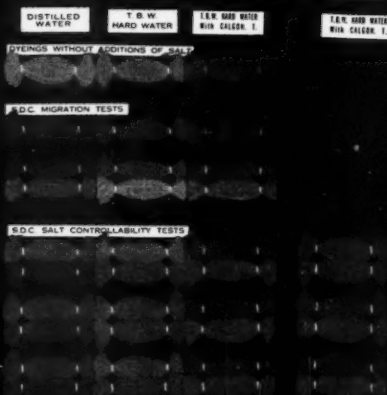
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# **CHLORANTINE FAST BLUE GLL200 DYED IN T.B.W. HARD WATER WITH CALGON T. AND IN WATERS OF LOWER HARDNESS**

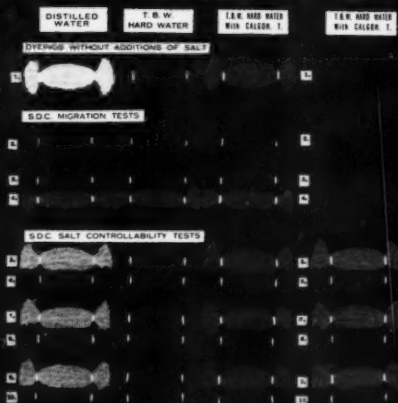


# **CHLORANTINE FAST BROWN BRLL 200** DYED IN 30 VOLTS 1 HOUR AT BOIL CLASS C

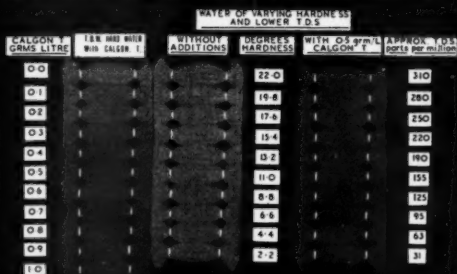


# **CHLORANTINE FAST BLUE GLL200**

DYED IN 30 VOLTS 1 HOUR AT BOIL CLASS B



# **CHLORANTINE FAST BROWN BRLL 200 DYED IN T.B.W. HARD WATER WITH CALGON T. AND IN WATERS OF LOWER HARDNESS**



# **CHLORANTINE FAST BROWN BRLL 200 BOILED UNDER REFLUX WITH CALGON T.**

AND SUBSEQUENTLY  
DYED IN 30 VOLTS 1 HOUR AT BOIL



# **CLASS A. & B. DYES AS MIXTURES**

DYED IN 30 VOLTS 1 HOUR AT BOIL

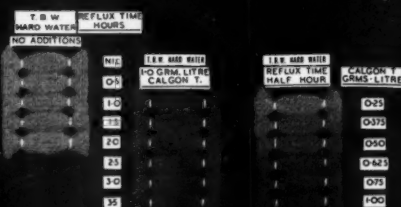
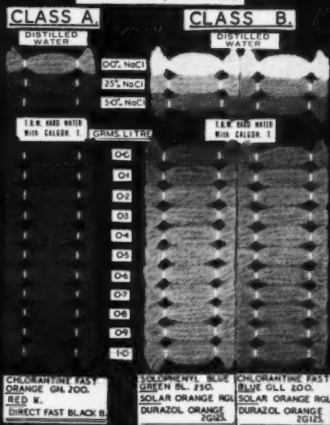


FIG. 2  
(T.D.S. = Total dissolved solids)  
(Key on p. 124)



(b) The second series, dyed in T.B.W. hard water, are with four exceptions very much fuller in shade, the exhaustion varying between 25% and nearly 50%. In the case of the four exceptions, viz.—

	Maker	Class	Fig.
Chlorantine Fast Brown BRL 200%	...	CAC	C 2
Solophenyl Olive BL	...	Gy	C —
Durazol Grey VG 150%	...	ICI	B —
Chlorazol Blue G 150%	...	ICI	A 1

the shades obtained in T.B.W. hard water are dull and dirty, due to the partial or complete precipitation of the dye by the calcium and magnesium in the hard water. In the case of Chlorazol Blue G 150%, the dye appears to be in solution yet little dyeing takes place, even in the presence of salt. The other three are obviously out of solution.

(c) In the third series, where 2 g. of Calgon T per litre has been added to T.B.W. hard water, the shades obtained are, with four exceptions, lighter than those dyed in T.B.W. hard water without this addition. The four exceptions are those mentioned above, which in T.B.W. hard water give dull and dirty shades but which give full shades when dyed in the presence of Calgon T.

The restraining effect of Calgon T in T.B.W. hard water varies with different dyes and, as will be shown later, differs according to the amount of Calgon T used.

**S.D.C. MIGRATION TESTS**—These tests follow the lines suggested by the Direct Cotton Dyes Committee\*. The tests were carried out in the following types of water—

- Distilled water
- T.B.W. hard water
- T.B.W. hard water containing 1 g. Calgon T per litre\*.

This is the measure by which a dye is placed in Class A of the S.D.C. classification. It is noticed that, whichever type of water is used for this test, the results differ very little indeed, and the addition of Calgon T does not appear to influence the migrating properties. There is, however, an interesting difference in behaviour of the dyeings made on 18 denier Fibro compared with that reported on cotton, and this will be discussed later.

**S.D.C. SALT CONTROLLABILITY TESTS**—These tests also followed the lines suggested by the Committee\*, and were carried out in the following types of water—

- Distilled water
- T.B.W. hard water
- T.B.W. hard water containing 1 g. Calgon T per litre.

In addition to the above, a further set of tests was made in T.B.W. hard water in which the salt additions of  $0.8 \pm 0.2\%$  made to the first dyeing were replaced by  $0.8 \pm 0.2$  g. of Calgon T per litre.

Salt controllability tests are prescribed to determine the degree to which the absorption of the dye can be controlled by means of salt added to the dyebath, and it is the test by which the dye is

placed in Class B or Class C of the scheme. Three pairs of shades are available for assessing the results. Here, again, the results on 18 denier Fibro differ from those reported on cotton, and these will be discussed later.

Salt controllability is the dyeing property most affected when direct dyes are applied in hard water. A study of the three pairs of shades available from this series of dyeings shows—

(i) In T.B.W. hard water all the first dyeings (with four exceptions) are considerably darker than those obtained under similar conditions in distilled water. (The four exceptions are those mentioned above which are precipitated in T.B.W. hard water.)

(ii) The majority of the first dyeings of the pairs are very much darker than the second dyeings.

Thus, many of the Class B dyes which on cotton give the same depth of shade with  $0.8 \pm 0.2\%$  common salt as they do with 20%, become Class C dyes when applied on 18 denier Fibro in hard water. As such they are grouped as dyes which cannot be controlled by additions of salt alone. In other words, the salt controllability of such dyes is either greatly diminished or lost entirely when applied in T.B.W. hard water.

However, when this test is applied in T.B.W. hard water to which has been added 1.0 g. of Calgon T per litre (in addition to the  $0.8 \pm 0.2\%$  common salt) there is a substantial reduction in the depth of shade obtained in the first dyeings, sufficient in many cases to restore the dyes to the correct Class B.

When the salt addition is omitted and in its stead  $0.8 \pm 0.2$  g. of Calgon T per litre is added to the dyebath, then the shades obtained are still lighter, indicating that a greater measure of control over the rate of exhaustion is obtained in this way. Dyeings containing 0.6 and 0.8 g./litre are lighter than those containing 1.0 and 2 g./litre.

#### EFFECT OF CALGON T WITH WATER OF LOWER HARDNESS

This is illustrated by dyeings made with two dyes which exhibit widely different behaviour in T.B.W. hard water, namely—

Chlorantine Fast Blue GLL 200 (Fig. 2)  
Chlorantine Fast Brown BRL 200 (Fig. 2)

(a) T.B.W. hard water with additions of 0.1, 0.2, 0.3, . . . 1.0 g. Calgon T per litre.

(b) Water of varying hardness, made by diluting T.B.W. hard water with additions of distilled water to give waters with the following degrees of English hardness and total dissolved solids (p.p.m.).

English Hardness (°)	Total Dissolved Solids (p.p.m.)
22.0	310
17.6	250
15.4	220
13.2	190
11.0	155
8.8	125
6.6	95
4.4	63
2.2	31

(c) Waters of varying hardness as in (b) each containing 0.5 g. of Calgon T per litre.

\* 1 g. per litre is the concentration of Calgon T which will maintain the dye in solution.

An examination of the dyeings made with the Blue GLL show in (a) that the maximum restraining influence is obtained with an addition of 0.5 g. of Calgon T per litre, and the shade given is comparable with that obtained in (b) in water of 6.6° hardness or 95 p.p.m. total dissolved solids and considerably lighter than the shade given in water of 11° hardness. In (c) the restraining power of Calgon T is shown to be effective in waters of lower hardness and even with water as low as 4.4° hardness is still quite marked.

With the Brown BRLL a reverse effect is observed. In (a) the solubilising effect of Calgon T first becomes evident at a concentration of about 0.5 g./litre, above which the shades become progressively fuller with increased additions of Calgon T. In (b) the effect of very low concentrations of calcium and magnesium on this very sensitive dye is shown by precipitation and dirty shades in waters above a hardness of 6-7°. In (c) the depth of shade obtained varies only in waters of 6-9°, where a slight increase is noticed, which suggests that at this concentration a near balance between the calcium (magnesium) and Calgon T is obtained, and "salting on" begins.

The results of these tests (Fig. 2) are shown graphically in Fig. 3 and 4, which illustrate the effects obtained more clearly.

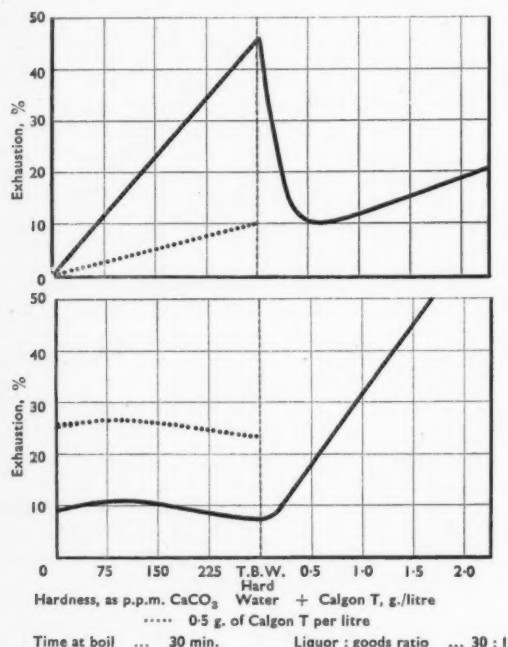


FIG. 3 and 4—Effects of Hardness and of Additions of Calgon T Exhaustion of Chlorantine Fast Blue GLL 200 and Chlorantine Fast Brown BRLL 200 respectively.

DIFFERENCES OBSERVED BETWEEN THE S.D.C. MIGRATION AND SALT CONTROLLABILITY TESTS CARRIED OUT ON 18-DENIER FIBRO AND THOSE REPORTED ON COTTON

MIGRATION TEST—Three reference standards have been chosen for this test, viz.—

	Makers	Fig.
(i) Direct Pink EG 400 ...	Gy	—
(ii) Chlorantine Fast Yellow SL ...	CAC	1
(iii) Durazol Blue 4R 200% ...	ICI	1

which when dyed on cotton give almost equality of shade after half-an-hour at the boil, and by virtue of this are placed in Class A of the scheme.

On 18-denier 8-in. Fibro none of these standards gives anything like equality of shade in this test. In the case of Direct Pink EG 400 and Durazol Blue 4R 200, at least one hour at the boil is required, and in the case of Chlorantine Fast Yellow SL, equality was not reached in 1½ hr.

A variation of the salt content between 7½% and 15% made little difference. Of the Class A dyes tested, the following gave near equality—

	Makers	Fig.
Rosanthere R ...	CAC	—
Chlorantine Fast Red K ...	CAC	—
Chloramine Fast Yellow 4GL ...	S	—
Chlorazol Yellow 6GS ...	ICI	—
Chrysophenine G ...	LBH	—

while others were not quite so good in levelling.

This difference in behaviour of the same dye on different fibres is of particular importance in the problem under discussion, for unless initial control over the "strike" and the rate of exhaustion is obtained, the unlevel results which may occur even with Class A dyes might prove difficult to correct, and a longer boiling time be required to produce uniformity.

SALT CONTROLLABILITY TEST—The reference standards for this test, viz.—

	Makers	Fig.
(i) Chlorazol Fast Scarlet 8B 125 ...	ICI	1
(ii) Direct Blue BT ...	CAC	—
(iii) Diphenyl Violet BV ...	Gy	1

when tested on cotton in distilled water, gave equality of shade between the first and second dyeings, with an addition of  $0.8 \pm 0.2\%$  common salt. On 18-denier 8-in. Fibro yarns all the reference dyes gave lighter shades under similar conditions; in fact, all the Class B dyes tested were found to give lighter shades than was anticipated.

Tests have been carried out to ascertain the percentage of salt required to produce equality of shade between the first and second dyeings when dyed on Fibro, and it was found that in the case of Direct Blue BT and Diphenyl Violet BV an addition of  $2.8 \pm 0.2\%$  was required, and in the case of Chlorazol Fast Scarlet 8B 125 up to  $4.4\%$  was needed to produce equality. Other dyes tested gave the following results—

	Makers	Salt (%)
Direct Sky Blue G ...	CAC	4.0
Chlorantine Fast Blue GLL 200 ...	CAC	5.8
Durazol Orange Brown 2RS ...	ICI	6.8
Chlorazol Blue B 500 ...	ICI	6.8

In the *Second Report of the Direct Cotton Dyes Committee*<sup>8</sup> it was pointed out that a larger percentage of salt was required for Fibro of 1.5 filament denier than for cotton. These results suggest that a still larger percentage of salt should be recommended for Fibro of higher filament denier.

## Properties of Calgon T in the Dyeing of Direct Dyes in Hard Water

### SEQUESTERING OR DISPERSING

Whether the property exhibited by Calgon T in the dyeing of direct dyes in hard water is due to its power to sequester or "lock-up" the calcium and magnesium salts or to its dispersing properties is a question which has been discussed at length. The manufacturers of Calgon T have stated that the sequestering power of this product is destroyed by boiling, and that after a solution of 0.2% Calgon T and 0.25% sodium chloride in T.B.W. hard water has been boiled for only thirty minutes no metaphosphate is left. In other words, the solution is no longer capable of sequestering any appreciable amounts of calcium and magnesium salts, but, owing to the presence of other phosphates, it is still capable of exerting dispersing power.

It was stated above that Chlorantine Fast Brown BRLL 200 is insoluble in T.B.W. hard water at the boil, but can be brought into solution by the addition of Calgon T, and successful bulk dyeings have been made with this dye at a 15:1 liquor: goods ratio, the liquor containing 2 g. of Calgon T per litre; the goods were entered at the boil, with additions of common salt or Glauber's salt, and boiling was continued for up to four hours. Additions of dye have been made to the bath, which have dissolved freely.

If Chlorantine Fast Brown BRLL 200 is brought into solution by virtue of the power of Calgon T to sequester the calcium and magnesium salts in the hard water, and if this power is due to the presence of metaphosphates, then it would be reasonable to assume that, by the destruction of the metaphosphates by boiling, the dye would fall out of solution.

### EFFECT OF REFLUX AT THE BOIL ON CALGON T WITH CHLORANTINE FAST BROWN BRLL 200 AND OTHER DYES

In order to study what happens to this dye—so sensitive to hard water—when subjected to prolonged boiling, the following tests were made (Fig. 2).

Controls were first prepared by dyeing 0.5% Chlorantine Fast Brown BRLL 200 in (a) distilled water and (b) T.B.W. hard water, both containing additions of 0.25, 0.50, 0.75, . . . 2.0 g. of Calgon T per litre. These dyeings show, in the case of distilled water, the "salting on" effect of Calgon T, and in T.B.W. hard water, the solubilising effect. The values of subsequent dyeings were judged by reference to these standards.

One gram per litre appeared to be the lowest concentration which would give, with T.B.W. hard water, the same clarity of shade as is obtained in distilled water.

Dyebaths of 150 ml. were prepared in T.B.W. hard water containing 1.0 g. of Calgon T per litre together with dye to produce a standard 1% dyeing on 5 g. of yarn. These dyebaths were then boiled under reflux for 1, 1½, 2, 2½, 3, and 3½ hr. respectively, after which the requisite volume (60 ml.) of distilled water was added, the baths were raised to

the boil, the dry yarn was entered and boiled for 30 min., and the hanks were washed off and dried. In the case of the dyeings refluxed for 3½ hr. the total boiling time would be 4 hr., and correspondingly less for the others.

On comparing these dyeings with the controls, very little difference could be observed; there appeared to be no deterioration of shade on prolonged boiling.

As no information could be gained from this series of dyeings, it was repeated, using only 0.5 g. of Calgon T per litre, and refluxing for periods of 0, 10, 15, 20, 30 min., 1, 1½, 2, 2½, and 3 hr. respectively.

An examination of these dyeings showed that after only 10 min. reflux, followed by 30 min. dyeing time, there were signs that the shade of the dye was being destroyed. Beyond that point and up to a period of 3 hr. reflux there appeared to be no further deterioration of shade.

The inference drawn from a study of these two sets of dyeings was that, while a Calgon T concentration of 1.0 g./litre was sufficient to protect the dyeing against the degradation caused by the hard water, 0.5 g./litre was insufficient to maintain the shade for as little time as ten minutes.

Further dyeings were therefore made using varying concentrations of Calgon T, and dyebaths were prepared containing 0.25, 0.375, 0.50, 0.625, 0.75, 0.875, and 1.0 g./litre, all of which were refluxed for 30 min. and subsequently dyed for a further 30 min. at the boil.

From this series it was judged that a Calgon T concentration of 0.625 g./litre or more was required to maintain the solubility of this dye for prolonged periods.

Dyeings made in T.B.W. hard water without additions of Calgon T were refluxed for ½, 1, 1½, 2, and 2½ hr. under similar conditions, and the only effect appeared to be that the dye was immediately precipitated and no appreciable dyeing took place.

Another example of the stability of Calgon T towards prolonged boiling is shown in a further series of dyeings made with Chlorantine Fast Brown BRLL in hard water containing graded additions of 0.25, 0.30, 0.35, . . . 1.0 g./litre.

In one case the stock solution of Calgon T used was freshly prepared, and in the other the 10% stock solution was previously refluxed for one hour. It was difficult to detect any difference in the two sets of dyeings.

This test has been carried out with another type of hard water, and with varying times of reflux, similar results being obtained.

Two further dyeings were made with Chlorantine Fast Brown BRLL—

- (a) In T.B.W. hard water + 2 g. Calgon T per litre
- (b) In T.B.W. hard water + 2 g. Calgon T + 1 g. soap per litre.

Both were refluxed for 2 hr. and subsequently dyed for 30 min. at the boil. The shades obtained in the two instances were identical, but the reflux had obviously destroyed the ability of the Calgon T to hold the soap in solution, though it had not affected the shade of the dye.



These tests indicate that Calgon T retains its ability to solubilise dyes such as Chlorantine Fast Brown BRLL under prolonged boiling, although its power to maintain a soap solution in hard water is destroyed by boiling.

Calgon T appears to form a complex salt with the calcium and magnesium salts of the dye, which is not broken down by prolonged boiling and, provided sufficient is present, the shade of which does not deteriorate.

The other property exhibited by Calgon T, and shown by this work, is that it has the power to restrain some direct dyes when applied in hard water, particularly Class B dyes, and in order to ascertain if this influence was in any way affected by prolonged boiling the following tests were made—

Dyebaths were prepared in—

- (a) T.B.W. hard water (no reflux)
- (b) T.B.W. hard water + 2 g. of Calgon T per litre (no reflux)
- (c) As (b) refluxed for 1 hr.
- (d) As (b) refluxed for 3 hr.
- (e) As (b) refluxed for 5 hr.

using the following dyes and dyeing for 30 min. at the boil—

Solar Orange RGL (S)  
Solophenyl Yellow FFL 250 (Gy)  
Durazol Orange 2G 125 (ICI)  
Solophenyl Blue Green BL 250 (Gy)  
Chlorantine Fast Blue GLL 200 (CAC)  
Chlorazol Blue B 500 (ICI)  
Chlorantine Fast Green 5GLL (CAC)

The results show that the restraining influence is maintained in varying degrees for up to 5 hr., and only with Chlorantine Fast Green 5 GLL is the shade as dark after 5 hr. boiling as that given in hard water without Calgon T.

#### OTHER PHOSPHATES

Other phosphate compounds have dispersing power but not the same ability to sequester calcium and magnesium salts as has Calgon T, and further tests were carried out with the following—

**DISODIUM HYDROGEN ORTHOPHOSPHATE**  $\text{Na}_2\text{HPO}_4$ , which has dispersing properties.

**TETRASODIUM PYROPHOSPHATE**  $\text{Na}_4\text{P}_2\text{O}_7$ , which is about one-ninth as effective as Calgon T in sequestering power.

**SODIUM TRIPOLYPHOSPHATE**  $\text{Na}_5\text{P}_3\text{O}_{10}$ , about one-half as effective as Calgon T in sequestering power.

**SODIUM TRIMETAPHOSPHATE**  $(\text{NaPO}_3)_3$ , without either dispersing or sequestering properties.

Using Chlorantine Fast Brown BRLL 200, dyeings were made in distilled water and in T.B.W. hard water, containing 2 g. of the above salts per litre, as well as Calgon T for comparison.

The dyeing with disodium hydrogen orthophosphate in hard water was not as full as that made with Calgon T and there was a dirty scum on the surface of the liquor. Trimetaphosphate also gave a dull dirty shade, while the tetrasodium pyrophosphate, although not as efficient as Calgon T in solubilising this dye, was an improvement over the first two mentioned. Of the four compounds, sodium tripolyphosphate gave results

nearest to those obtained with Calgon T, but there was a tendency to cloudiness in the dye bath and depth of shade was lacking.

Similar results were obtained with Durazol Grey VG 150, a dye which behaves much like Chlorantine Fast Brown BRLL in hard water.

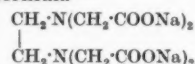
These compounds have also been tested with other dyes to check their varying efficiency as restraining agents in T.B.W. hard water. The results obtained do not compare favourably with those obtained with Calgon T.

Sodium tripolyphosphate gave results close to those of Calgon T when used with Chlorantine Fast Brown BRLL, and in order to ascertain if this salt would withstand prolonged boiling and still retain its sequestering power, a series of dyeings was made in T.B.W. hard water containing 0.25, 0.375, 0.5, . . . 1.0 g. of tripolyphosphate per litre, each being refluxed for 30 min. before being dyed for a further 30 min. at the boil. The shades obtained were true but lighter than those obtained in a similar range dyed with addition of Calgon T, and it was estimated that 1 g. of tripolyphosphate per litre was required to produce results comparable with 0.625 g. of Calgon T per litre, which is in keeping with the statement above—that this product is about half as effective as Calgon T in sequestering power.

#### OTHER SEQUESTERING AND DISPERSING AGENTS

Three other compounds have been tested, in each case at a concentration of 2 g./litre, with the results indicated below.

"SEQUESTERING AGENT A"—A sample of this substance, of formula—



similar to Trilon (IG), was supplied privately. It has powerful sequestering properties for calcium and magnesium salts in water. When used in T.B.W. hard water with Chlorantine Fast Brown BRLL it is ineffective; the alkalinity of the product destroys this dye in both distilled and hard water. When tested with Chlorantine Fast Blue GLL 200 it is effective as a restraining agent for a very short time, but the alkalinity affects the shade of this dye on prolonged boiling.

**IRGALON BT (Gy)**—A sequestering agent referred to in the maker's literature as an antidote to some undesirable metal effects, and stated to react with calcium and magnesium salts found in water to form water-soluble complex salts. With Chlorantine Fast Brown BRLL the effect of Irgalon BT is similar to that of "Sequestering Agent A", i.e. the shade is destroyed by the alkalinity\*. With Chlorantine Fast Blue GLL, Irgalon BT acts as a very strong salting-on agent, full shades being obtained, possibly due to the effect of the Glauber's salt used for standardising this product. It is not, therefore, effective as a restraining agent in hard water.

\* It has been suggested that the destruction of the shade may, in this instance, be due to the sequestration of copper from the molecule of the dye, resulting in a product of inferior fastness. The shade obtained fades within a few hours.



IRGASOL DA (Gy)—Marketed as a powerful dispersing agent. With Chlorantine Fast Brown BRLL in distilled water it acts as a salting-on agent, but this dye is not held in solution in T.B.W. hard water by Irgasol DA. With Chlorantine Fast Blue GLL 200 it is not effective as a restraining agent but acts as a powerful salting-on agent both in distilled and in T.B.W. hard water. This, again, is probably due to the effect of standardising diluent.

#### DISCUSSION OF RESULTS

Let us briefly review the results of the experiments made with other sequestering and dispersing agents in conjunction with the properties exhibited by Calgon T in the earlier trials, viz.—

(a) Used with dyes which are insoluble in T.B.W. hard water, or are precipitated by the calcium and magnesium present, thus giving little or no dyeing, irrespective of the sodium chloride concentration, Calgon T aids solubility and promotes dyeing.

(b) Used with dyes which are so sensitive to the large amounts of electrolytes present in T.B.W. hard water that they give a heavy "strike" in the absence of sodium chloride, Calgon T acts as a restraining influence and reduces the rate of exhaustion.

Chlorantine Fast Brown BRLL 200 has been used as a reference standard for type (a) and Chlorantine Fast Blue GLL 200 as a reference standard for type (b).

The dispersing agents tested were disodium hydrogen orthophosphate and Irgasol DA, neither of which will hold Chlorantine Fast Brown BRLL in solution or restrain Chlorantine Fast Blue GLL.

The sequestering agents tested were "Sequestering Agent A", sodium tripolyphosphate, and Irgalon BT. The second is effective in giving similar results to those obtained with Calgon T to a degree comparable with its efficiency as an agent for locking up the calcium and magnesium salts, i.e. about one-half that of Calgon T; while the other two are both ineffective owing to their alkalinity, which affects the shade of the two dyes chosen as reference standards.

It is not to be assumed from the above statements that Irgalon BT is ineffective as an agent for locking up calcium and magnesium ions. On the contrary, under some conditions it is a valuable sequestering agent, particularly against iron ions, but when used with direct dyes which are sensitive to alkalinity it will affect the shade if boiling is prolonged, whereas Calgon T exerts a buffer action and will neutralise alkalinity developed when waters containing temporary hardness are boiled.

It would seem, then, that Calgon T does not act in quite the same way as other well known sequestering and dispersing agents, but in its original form as well as after prolonged boiling, when it is presumed to break down, it appears to form a complex which either promotes (Chlorantine Fast Brown BRLL) or inhibits (Chlorantine Fast Blue GLL) dyeing according to the solubility of the calcium or magnesium salt of the particular dye. It has been shown that its power to inhibit or

promote dyeing is as good after four hours' boiling as it is after two minutes'.

It is outside the scope of this paper to attempt to offer any further explanation for the favourable effect of Calgon T with the dyes tested compared with other products having similar properties, but there is no doubt about its value as an assistant in the dyeing of direct dyes under the difficult conditions outlined at the beginning of this paper.

Perhaps this small contribution to the mass of literature available on the dyeing of direct dyes will be of sufficient interest to provoke some discussion, and possibly induce other workers to extend this investigation to the full range of direct cotton dyes.

#### Application of Results to the Practical Dyeing of Fibro Yarns in Hard Water

##### ADVANTAGES GAINED BY USING CALGON T

In summarising this work and translating its value to the bulk dyeing of Fibro yarns in hard water, the advantages to be gained can be related to the limitations imposed by the hard water, viz.—

(a) The choice of dye from the direct cotton range is restricted to those which are freely soluble in hard water and are not precipitated by prolonged boiling.

(b) The use of soluble Class A dyes, where a heavy "strike" can be corrected by the good levelling and migrating properties of this class. Only a moderate wet fastness is obtainable with this class.

(c) The risk of a heavy "strike" and consequent initial unevenness when Class B or Class C dyes are used, a fault not easily corrected. An improved wet fastness is obtained with Classes B and C.

(d) Dyeings made in hard water leave the yarn harsh and dusty when dried, due to the precipitation of temporary hardness. This finely divided calcium carbonate is held in the yarn after dyeing. The use of Glauber's salt for salting also causes dust due to the formation of calcium sulphate.

(e) Some types of hard water, particularly those having a high temporary hardness, develop alkalinity on boiling owing to the liberation of carbon dioxide. Many direct dyes are so sensitive to alkalinity that true shades are not obtained. This also happens in some softened water.

Calgon T counteracts the above limitations as follows—

(a) Calgon T enables all direct dyes to be dissolved quite readily in hard water, the concentration required being dependent on the solubility of the calcium or magnesium salts of the particular dyes.

(b) With some Class A dyes Calgon T does assist in controlling the rate of exhaustion.

(c) Those Class B dyes which "strike" heavily in hard water and become Class C dyes can be restored to Class B by the use of Calgon T in small amounts. Control over the rate of exhaustion can be regained, and the shades built up gradually.

(d) The addition of Calgon T prevents the precipitation of temporary hardness and leaves the yarn soft.

(e) Calgon T develops acidity on boiling, and this is sufficient to buffer the solution and counteract the alkalinity developed by some waters, thus protecting the shade.

(f) It has been found that an addition of 0.5 g./litre to Manchester tap-water (25 p.p.m.) has a decided restraining influence on the "strike".

#### PRACTICAL APPLICATION TO LARGE-SCALE WORK

These notes have been compiled as a result of experience gained in the dyeing of large weights of Fibro carpet yarns with direct dyes in hard water, with the equipment available in the average carpet wool yarn dyehouse, using the Calgon T method of controlling the rate of exhaustion.

It is assumed that the usual precautions will be taken to ensure that the vats used are clean and free from acid. Staybrite machines of the Hussong or Pegg Pulsator type are quite satisfactory, but wooden machines which have been used for acid dyeing for long periods are liable to cause trouble due to the bleeding of acid from the wood.

Viscose swells quite considerably when wet, and allowance must be made for this when packing the machine. Care should also be taken to see that the tie-bands are sufficiently loose to allow for this swelling. The machines mentioned above will give excellent results. Lots of 1200 lb. of 90-in. hank, 2/12 18 denier, jute-spun Fibro yarns have been satisfactorily dyed in a Longelose Hussong machine with a liquor capacity of 1880 gal. at working level. This represents about 7 lb. of yarn per foot of pole space with a liquor : goods ratio of 15 : 1. If 72-in. hanks are used, then the capacity of the vat will be reduced to about 950 lb. of yarn.

Fibro yarns are heavy, and the hanks are inclined to pack themselves into individual packages, so that an underloaded machine will lead to channelling, while an overload will be difficult to penetrate.

**SCOURING**—The jute-spun yarns as used for the experiments mentioned, and similar to those which are being received in the industry at the present time, will not require to be scoured, but condenser- or worsted-spun yarns containing oleine or other oils must be scoured and well washed before dyeing. This is best carried out in the dyeing machine by treating with, say, 2 g. of soda ash per litre together with one of the synthetic detergents at the boil, and then washing at the boil. Hard water should be treated with Calgon T. It is not advisable to pass Fibro yarns through squeezing rollers in the manner customary with wool yarns in the carpet industry, as the heavy rollers cut wet viscose very easily.

**HYDROEXTRACTING**—Stains can result from hydro cages which are not free from acid, particularly copper cages. Prolonged treatment at high speeds should be avoided; a light hydroextraction is usually sufficient.

**DYEING** should be carried out at as low a temperature as possible. High temperatures produce a harsh yarn as well as temporarily affecting the

shade of some dyes. This change of shade is more marked with direct cotton dyes than it is with acid dyes. Matching threads should be well cooled before examination.

**DYEING**—It is strongly recommended that shades should be matched in the laboratory before proceeding with bulk work. Very good results can be obtained if attention is paid to detail: weighing, measuring, timing, etc. must be accurate, and in particular the liquor ratio must be as near to that of the large-scale machine as possible.

#### DYES AND DYEING PROCEDURE

The choice of a dye for any particular purpose will depend upon the fastness requirements and the cost allowed. It is unlikely that shades required for the carpet industry can be obtained from single dyes, and care should therefore be taken to ensure that dyes chosen for mixtures have similar fastness properties and that they dye the fibre as nearly as possible at the same rate. This is not a simple matter, and advantage should be taken of the information supplied by the dye manufacturers, and that contained in the papers already referred to, regarding the fastness and dyeing properties of direct dyes.

The fastness properties of direct dyes are not in any way affected by the use of Calgon T in controlling the rate of exhaustion in hard water, but the method of application depends on the class of dye being employed.

The first consideration is that the dye must be brought into solution. The amount of Calgon T required will vary according to the dye used with different types of hard water.

It is now an established practice to enter rayon yarns into the dyebath at the boil and to keep the liquor at that temperature. Whittaker<sup>6</sup> points out that at 90°C. the viscosity of water is low in comparison with its viscosity at low temperatures, and the freest circulation is therefore obtained at high temperatures.

If Class A dyes are chosen and the dye made soluble, then from a dyeing point of view there is little else to worry about. A bad "strike" can be corrected by the good migration properties of this class of dye, but it should not be overlooked that from the migration tests carried out on 18-denier Fibro a longer time at the boil is required to produce equality than is required for cotton. Class A dyes should be entered at the boil, and advantage should be taken of the control offered by Calgon T rather than reliance placed upon a long boil to correct initial unevenness.

Class B offers a wider selection of dyes having the fastness properties required for carpet yarns, and a choice can be made from this group to suit most requirements. Their application, however, needs greater care if level results are to be obtained, since they do not migrate easily and must therefore be applied evenly from the commencement of the dyeing. It is with Class B dyes that Calgon T is most valuable.

In order to reduce the "strike" and the rapid exhaustion obtained in hard water, additions of

Calgon T are made during the boiling up of the dye-bath, and from tests made the concentration which gives the maximum restraining power with Class B dyes is 0.5-0.7 g./litre, but if the concentration of Calgon T required to dissolve the dye is greater, then that should be the minimum used. If the yarn or package appears difficult to penetrate, it is advisable to take the maximum precautions by commencing the dyeing with only sufficient Calgon T to dissolve the dye and obtain the greatest restraining effect, thus enabling the liquor to penetrate the mass of yarn, and preventing the salting of a heavy layer of dye on the surface of the fibre. There appears to be no real value in using less than 0.5 g./litre, though this may be more than is required to obtain solubility of the dye. After running the machine for 5-10 min., further additions of Calgon T should be made, up to the amount required to sequester all the calcium and magnesium present in the water. This will ensure that the yarn is soft and free from dust. Regular additions of salt can now be made to build up the shade. The quantity and frequency of the additions will depend upon the salt sensitivity of the dye, and a great deal of information has been published on this point.

The above represents the method of obtaining the best possible control over the rate of exhaustion when using hard water, and is in fact an extreme which should not be necessary except with packages or hard-twisted yarns. The restraining influence of a Calgon T concentration of 2 g./litre (for T.B.W. hard water) should be adequate to prevent a too rapid exhaustion of the Class B dyes, and the dyeing can be safely started with that amount. A little experience will enable the dyer to judge what liberties he may take with the process and the particular dye he is employing.

Class C dyes in general require temperature control as well as control by Calgon T, and dyeing should therefore be commenced with the maximum Calgon T concentration at a low temperature. Chlorantine Fast Brown BRLL (Class C) has been applied to Fibro commencing at the boil, with quite satisfactory results, and is possibly a borderline B-C dye.

Calgon T is supplied packed in cotton bags containing 25 lb. each, and it is easily dissolved by hanging the bag in the dye-bath while boiling up. Small additions are better added from a previously prepared stock solution.

The author wishes to express his thanks to the Directors of Messrs. T. Bond Worth & Sons Ltd. for providing the facilities for the work to be carried out, and for permission to publish this paper.

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Finally, he wishes to record his appreciation of the vast amount of experimental work which has been carried out with such infinite patience by Miss Z. Corrington.

#### DYEHOUSE DEPARTMENT

T. BOND WORTH & SONS LTD.  
SEVERN VALLEY MILLS  
STOURPORT-ON-SEVERN

#### References

- <sup>1</sup> Boulton and Morton, J.S.D.C., 56, 145 (1940).
- <sup>2</sup> Whittaker, *ibid.*, 54, 259 (1938).
- <sup>3</sup> Whittaker, *ibid.*, 57, 145 (1941).
- <sup>4</sup> Whittaker, *ibid.*, 58, 253 (1942).
- <sup>5</sup> Boulton, *ibid.*, 60, 5 (1944).
- <sup>6</sup> Whittaker, *ibid.*, 60, 109 (1944).
- <sup>7</sup> Lemin, Vickers, and Vickerstaff, *ibid.*, 62, 132 (1946).
- <sup>8</sup> *First and Second Reports of the Committee appointed by Council to discuss the Dyeing Properties of Direct Cotton Dyes* (reprinted from J.S.D.C., 62, 280-285 (1946), and 64, 145-146 (1948)).

#### Discussion

Mr. D. B. McPHERSON: Has Mr. Campbell done any work with soft water comparable with his experiments on dyeing in hard water? Does he claim that there is any definite advantage in using Calgon T in soft water?

Mr. CAMPBELL: We have not done any large-scale work in soft water. Experimental work indicates that Calgon T acts as a salting-on agent in soft water, but there is an advantage to be gained where soft waters develop alkalinity on boiling, since Calgon T acts as a buffer and protects dyes which may be sensitive to alkalinity.

Mr. J. C. HAWLEY: Has Mr. Campbell done any comparative tests with Calgon B as he has with Calgon T? Is there any reason for keeping expressly to Calgon T? Has he done any work with silicates?

Mr. CAMPBELL: Regarding Calgon B, which is Calgon T buffered with soda ash, in the case of those dyes which strike heavily in hard water the addition of soda ash will tend to increase the strike, rather than assist in restraining the dye. As far as silicates are concerned, we have not done any work in this direction, but the same remarks would apply to these compounds as to soda ash. There appears to be no reason why silicates should sequester.

\* This question has subsequently been followed up, and it has been found that sodium silicate will not hold Chlorantine Fast Brown BRLL in solution in very hard water.

Mr. H. HAMPSON: I confirm Mr. Campbell's observation that direct dyes take longer to level on 18-denier Fibro than on cotton. I am at present doing some work on this question, using all deniers up to 50, and the results will be published when the work is complete. The finer deniers are harder to dye than the coarser probably because the finer deniers tend to cake more than the coarser; therefore there is not the same easy penetration, and the initial absorption will be faster with the finer deniers. Has Mr. Campbell any experience with the finer deniers?

Mr. CAMPBELL: Although not an ideal carpet yarn, we have dyed large quantities of 4½-denier



Fibro and in some instances have experienced difficulties. It does lie heavily on the sticks, and the hanks have a tendency to pack themselves into individual packages, which can be difficult to penetrate, but by controlling the rate of exhaustion good results have been obtained. The salt controllability tests we have carried out and shown in the pattern cards support Mr. Hampson's statement that the coarser deniers do not dye as heavily as the finer deniers.

Mr. G. ROBINSON: In the dyeing of Fibro in the ordinary way it is usual to use dyes with similar diffusion rates. Is it possible to mix Classes A, B, and C indiscriminately?

Mr. CAMPBELL: We have taken liberties by mixing the classes of dyes. In the case of a mixture of, say, a Class B dye with a Class A dye, providing precautions are taken to ensure the level application of the Class B dye, then the Class A will take care of itself. It should not, however, be overlooked that the Class A dyes do take rather longer to level on 18-denier Fibro and should therefore be applied with care. We have used Class A dyes for shading Class B or Class C dyes where the quantity required would not affect the wet fastness of the dyeing and had the requisite light fastness. It is easier to match dyeings when all the dyes have similar diffusion rates.

## MANCHESTER SECTION

Meeting held at the Gas Department Showrooms, Manchester, on 18th March 1949  
Mr. J. G. EVANS in the chair

### Some Aspects of Printing Thickenings (especially Starch Thickenings)

J. ZONNENBERG

#### I—Introduction

The functions of a thickening agent are very important and various, the quality of the resulting print depending largely upon the thickening agent. The depth, the brightness of the colours, and especially the sharpness and smoothness of the print are influenced or even determined by it. The different thickening agents show considerable variation as to their suitability for the various applications, and the non-availability of a certain thickening agent may prevent a certain pattern or article from being printed at all.

Our comparative ignorance of the scientific basis of the application of thickening agents is probably due to the late development of the sciences of colloid and especially macromolecular chemistry.

This paper will deal mainly with the application and technical examination of thickening agents

based on starch, but firstly a short summary of modern ideas on the structure and properties of starch will be given.

#### II—Structure and Properties of Starch and its Components

Starch and other thickening agents are highly polymeric carbohydrates, their molecules consisting of several hundred or even a thousand simpler units. The structure of these macromolecules is responsible for their ability to bind or thicken large quantities of water.

Both starch and cellulose consist of macromolecules of polyanhydroglucose. Unlike cellulose, starch is not a homogeneous substance, but is generally regarded as containing two different components, viz. *amylose*, consisting of linear polyanhydroglucose chains (Fig. 1), and *amylopectin*, consisting of highly branched chains (Fig. 2).

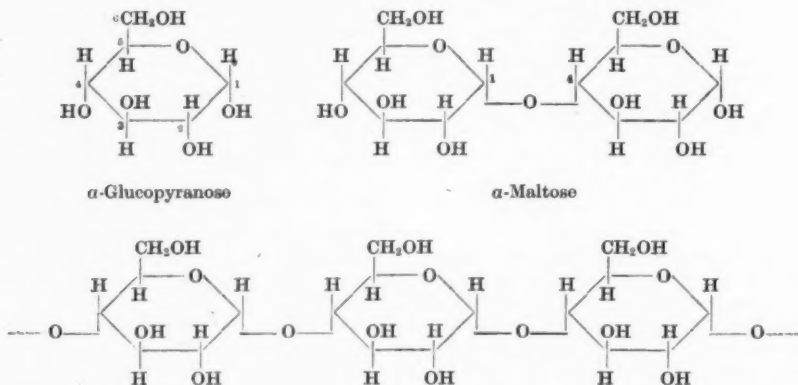
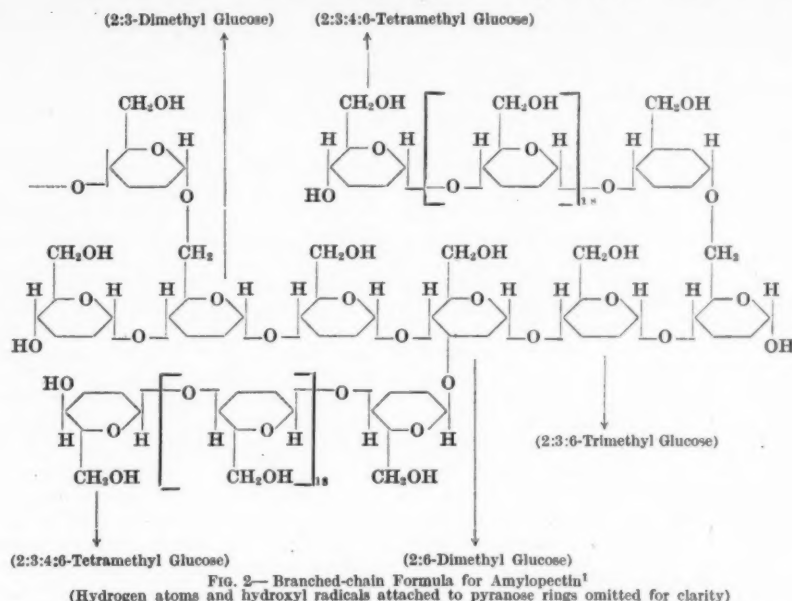


FIG. 1—Starch



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FIG. 2—Branched-chain Formula for Amylopectin<sup>1</sup>

The properties of the two components are compared in Table I.

TABLE I Properties of Components of Starch		
Property	Amylose	Amylopectin
Molecular weight...	Comparatively low	High
Degree of polymerisation (glucose units)	200-400	> 1000
Chain branching...	Linear, unbranched	Highly branched
Thickening power	Very low	High, as water bound in the intramolecular spaces within the branched structure
Tendency to crystallise	High, as linear molecules readily oriented in parallel (hence retrogradation phenomenon of starch solutions due to crystallisation of amylose)	Low, because of branched structure
Stability of aqueous solutions	Low	Fairly high
Colour with iodine	Deep blue	Red or violet

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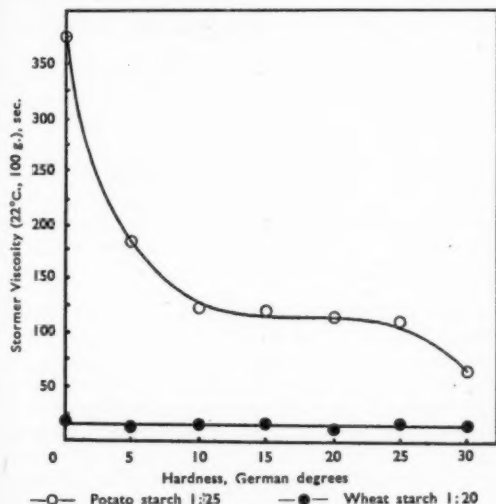


FIG. 3

Another difference is the fact that amylopectin contains phosphorus, whereas amylose contains none. In the kinds of starch originating from tubers and roots the phosphorus is linked to the glucose chain as a mono-ester; with those originating from cereals this is not the case, and according to Posternak<sup>2</sup> it is present in the form of phosphatides, and so blocked. Thus in the first case (potato starch) two phosphoric hydrogens are free. The amylopectin or amylophosphoric acid is, therefore, an acid of high molecular weight with colloidal properties ("colloid acid"), and this acid can give salts with calcium and magnesium ions. Hence results the influence of hard water on the swellability of certain types of starch, as shown in Fig. 3. From Table II it is clear that the quantities of phosphorus in the various kinds of starch differ greatly.

TABLE II  
Source of Starch      Phosphorus Content  
(% P<sub>2</sub>O<sub>5</sub>)

Potato ...	0.175
Manioc ...	0.017
Wheat ...	0.104
Maize ...	0.045
Rice ...	0.015

### III—Starch as a Thickening Agent

#### (a) GELATINISED STARCH

When a suspension of starch in water is heated, the granules swell, up to a 100 times their original volume. It appears that one of the components, viz. the amylose, dissolves in water; while the remainder, the amylopectin, which in some measure retains the form of the granule, only swells. Properly speaking, the resulting starch paste consists of swollen amylopectin particles suspended in an amylose sol.

It is well known that a paste of one type of starch gels or thickens more quickly than one of another type; e.g. solutions made from maize starch or rice starch gel much quicker than those

from potato starch. This difference in colloidal behaviour of solutions of the various types of starch depends both on a difference in degree of polymerisation of the amylose and on a difference in size and degree of branching of the amylopectin molecules.

It follows from the above that the congealing of a starch paste is mainly a consequence of the crystallisation of the amylose fraction. This thickening can be accelerated by addition of acids or retarded by alkalis.

The differences in viscosity of the starches are associated with differences in morphological structure of the granules. Potato starch granules, for example, are capable of swelling up a hundredfold without falling apart. Grains of rice starch, on the other hand, swell only thirtyfold. Starch granules consist of both amorphous and crystalline parts, the presence of the latter being shown by the double refraction and the X-ray diffraction pattern of the granules. The crystalline part consists of parts of chains belonging to different starch macromolecules, which form a rib-like structure; and the same macromolecule may partly crystallise in different sections of its chain with other macromolecules, these small areas of strong orientation being termed *crystallites* (or *micelles*). A starch granule can be deformed elastically, because the crystallites are connected by free sections of the macromolecular chains. This concept also explains why starch granules when treated with dilute acids or saliva become brittle and completely disintegrate. First the free parts of the chains (the amorphous part) are affected and hydrolysed, whereby the micelles are loosened and the granule disintegrates.

This view of the structure of the starch granule, as consisting of crystalline and amorphous parts, the latter constituting an elastic binder between the crystallites, and thus the whole granule consisting, so to speak, of a three-dimensional network, in which the junction points represent the crystallites, explains in a simple way the swelling phenomena and the formation of a viscous, colloidal solution when starch granules are heated with water. In this case there will first be an *intermicellar* swelling of the parts consisting of free chains, and only when the crystallites are about to "melt" does *intramicellar* swelling take place. The gelatinisation phenomenon is therefore, properly speaking, nothing but the melting of the crystallites, after which the starch macromolecules dissolve.

A difference in structure of the three-dimensional network, constituted by the large and partly crystalline amylopectin molecules, therefore results in a difference in viscosity of the various starches.

If the structure of the starch granule is completely destroyed, as in the preparation of cold-swelling starch, when the amylopectin layers also disappear, the gelling power, i.e. the ability to crystallise, is quite lost, and behaviour rather like that of the natural gum thickenings results.

#### (b) STARCH AS A THICKENING AGENT FOR TEXTILE PRINTING

Despite its shortcomings, starch is one of the most important, if not the principal, ingredient in

thickenings. Starch products are inexpensive, and under normal conditions can be easily obtained anywhere and in a very pure form. Of all thickening agents it gives by far the highest colour yield. On the other hand, the natural gum solutions (gum arabic, etc.) are more stable and possess better printing properties; they have a better levelling power and can be more easily washed out than starch thickenings. But the gum solutions give a very low colour yield, and coagulate with various mordants. Attempts have therefore been made to improve the properties of starch by all types of chemical attack, the starch molecule becoming smaller as the chains are broken down. First of all soluble starch is obtained, and afterwards dextrin (British gum). The products obtained have a more gummy character, their levelling power is better, and they are more easily washed out than untreated starch.

Against these advantages in relation to starch, one has to put a few important disadvantages—

(i) The thickening power is considerably decreased; i.e. in order to make a thickening of the same consistency as one of starch, the amount of dry material to be used should be 3-4 times as great.

(ii) The products have developed reducing properties, owing to which they cannot be used for various applications (e.g. with azo dyes).

(iii) They show very strongly the phenomenon of setting into a solid mass in consequence of crystallisation.

(iv) They give a much lower colour yield.

(v) They give in many cases (i.e. with acid printing pastes) a less sharp print.

We made attempts to evolve a new method of giving starch gumlike properties without modifying it too much, by which method the disadvantages of the low thickening power, the reducing properties, and the low colour yield, which are peculiar to the various types of British gum, would be avoided. These new ideas resulted in the Solvitex products, invented some fifteen years ago. These thickening agents, which, in contrast to other starch derivatives, swell even in cold water, have practically lost their crystallising power (and do not, therefore, gel or stiffen after standing in the cold for a long time), and thus possess another property making them resemble the natural gums. They have little or no reducing action and give a high colour yield, as compared with the natural and British gums.

In the preparation of Solvitex, starch is mixed at very high temperatures with far less water than that required to occupy the volume of the swollen starch granules. Simultaneous application of high pressure presses the swollen granules together with great force. As the mass is rolled out to a filmlike layer, the little water present soon evaporates at the high temperature. In this way the crystal structure disappears. The starch has become amorphous, as the amylose and the amylopectin have melted together to one mass. Under the microscope, therefore, this starch product looks quite different from ordinary starch (Fig. 4). Absence of a black cross when observed through crossed nicols confirms

the disappearance of crystalline structure, which should account for the power to swell in cold water.

However, the rinsibility of the Solvitex products was insufficient if printed on certain fibres, e.g. rayon, which are not subjected to such severe aftertreatment as cotton. Research was, therefore, specially concentrated on improving the rinsibility of the Solvitexes. This investigation is now practically complete, and has led to many new products, considerably surpassing the Solvitexes as regards printing properties.

If starch is etherified (or esterified) under certain conditions, its hydrophilic properties are greatly affected, its solubility being considerably increased. The products were termed *Solvitoses* (starch ethers). Compared with technical starch products which have not been etherified, such as the thin-boiling starches, cold-swelling starches, and British gums (dextrins), the cold-water-soluble starch ethers (*Solvitoses*) possess various interesting properties, and thus have certain advantages for various purposes. They are, *inter alia*, noted for a better solubility and, when dissolved, do not show any phenomena of retrogradation, crystallisation, or gelling, but a greater resistance to micro-organisms. The stability of the starch ethers should be ascribed mainly to the etherification of the amylose fraction of the starch, which diminishes the probability of association and crystallisation of amylose molecules.

In the preparation of *Solvitoses* three main methods of etherification have been followed, with the production of starch ethers containing hydroxyl, carboxyl, and sulpho groups respectively.



FIG. 5—Stormer Viscosimeter

We have employed the Stormer viscosimeter to test the suitability of printing colours and thickening agents. At the left-hand side (Fig. 5) the instrument is provided with a cup (test cup) placed in a water-bath, which can be kept at a fixed temperature by means of an electric thermoregulator. In the cup a thermometer can be placed. The cup with the water-bath can be raised until it surrounds the cylinder shown in the drawing. The cylinder is fixed to a rod which can be rotated by means of the

weights hanging on a hook attached to the end of a thin silk cord, which is wound round the pulley on the top of the instrument. The screw on the right-hand side is a brake, with the aid of which the transmission can be stopped. The pulley has a free-wheel, so that the cord can be wound up again, after it has run down, without causing the transmission to function. The number of rotations of the cylinder is registered by a meter.

When the cup has been filled with the thickening or printing colour to be examined, the cylinder can be made to rotate by releasing the brake. The time  $t$  required for one hundred rotations is noted. The instrument is adjusted to pastes of varying resistance by changing the weights  $W$  suspended from the thread, from 50 to 1000 g. in steps of 50 g. The number of rotations of the cylinder per second per unit applied weight is a measure of the fluidity  $F$  of the thickening—

$$F = \frac{100}{t \times W}$$

This is the reciprocal of the viscosity. Thus the times required for a hundred rotations with a given load are proportional for the viscosities of the liquids surrounding the cylinder.

This instrument has already been employed in the study of the properties of various printing pastes<sup>3</sup>.

### Stability of Thickenings

The difficulty in meeting the requirements for a thickening agent for printing lies in the large number of factors to which stability is necessary. Thus at present no thickening agent is known proof against all additions which are possible from the colourist's point of view.

#### 1. EFFECT OF MECHANICAL STIRRING ON THICKENING POWER

A printing paste, the thickening power of which is greatly diminished by mechanical stirring, gives rise to all kinds of inaccuracies. Thus, on the printing machine the printing colour is swiftly rotated in the colour boxes, especially at high speeds of the driving mechanism. If the paste is thinned down by this rotation, the result of the print is greatly affected. In the case of very fine patterns, such as piccos and similar discharge prints on dark-dyed grounds, this is disastrous.

In order to investigate this effect, various thickenings were brought to the same viscosity and stirred in a metal cup by means of a glass stirrer driven by an electric motor at maximum speed for 5, 10, 15, . . . 60 min. Immediately after finishing the stirring, the viscosity was ascertained again. Although the demands made on the thickenings by this method were higher than in practice, a good comparison of the stability of one thickening agent with that of another was obtained.

It will be seen (Fig. 6) that in this respect wheat starch shows the worst behaviour, while gum arabic is the best. The drop in viscosity of starch thickenings is the phenomenon of *thixotropy*. This is no doubt connected with the heterogeneous structure of a starch thickening, in which the greater part of the starch paste is in a swollen

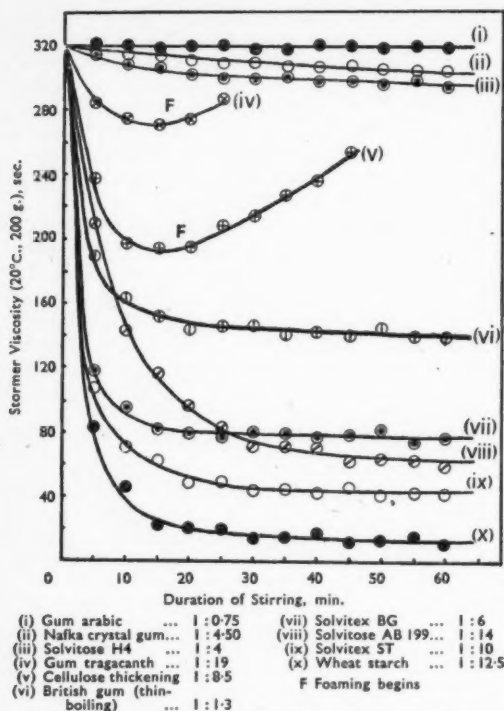


FIG. 6—Influence of Mechanical Stirring on Thickening Power

and not a colloiddally dissolved state. The mechanical stirring causes a part of the thickening in the gel form to pass into the sol state, which results in a lower viscosity. On subsequent standing, this may return from the sol to the gel state, i.e. the higher viscosity may partly return, but so long as the mechanical influence continues, as is the case on the printing machine, the lower consistency also remains. This unfavourable property, and the bad stability connected with it, should not be found with good thickening agents. We can therefore understand also why colloiddally dispersed gum arabic, i.e. in the sol state, is practically immune to mechanical influences.

These experiments show also that the cellulose thickening and gum tragacanth, after first decreasing in viscosity, on continued stirring increase in viscosity. This is due to the fact that air is stirred in, is retained by the thickening, and causes foaming. This is another inconvenience, which is undoubtedly no less troublesome, for it causes the print to turn out far too pale. Solvitose H4 appears to be by far the best of all starch products, and is almost as good as gum arabic.

## 2. MUTUAL INFLUENCE OF THICKENING POWERS OF AGENTS IN MIXTURES

It is customary in practice to combine various thickening agents, but so far little consideration appears to have been given, either in practice or in the literature, to what happens in such cases. How divergent opinions on this point appears from the following two quotations. According to Knecht and Fothergill<sup>4</sup>—

Gum Senegal, Gum Arabic, Gum Gedda and other thickenings of the same family, are best used by themselves. When mixed with starch, flour or Gum Tragacanth they break up the thickening, deprive it of its "body", destroy its nature and convert it into a slimy mixture, very apt to separate into its constituents during the printing process, and rarely or never giving satisfactory results, even if it happens for the purpose of retaining its original consistency.

In contradiction to the above, according to Haller<sup>5</sup>—

We should look upon a starch-gum thickening as the best substitute for starch-tragacanth. The starch in the gelatinised state takes over the part of the swollen parts of the tragacanth solution and is also the bearer of the coarse capillaries and hollow spaces. The gum in the said mixture with a much finer structure plays the part of the water-soluble viscous part of the tragacanth. It is striking that, in spite of this, the gum-starch thickenings in general have found little application in textile printing.

In order to investigate the effect of mixing different thickenings, we started again from thickenings of the same Stormer viscosity, carefully neutralised in advance, so as to eliminate the influence of any differences in the pH of one thickening on the viscosity of the other when mixed. Three graphs were drawn. The first (Fig. 7) shows the effect of mixing gum arabic with increasing quantities of two other thickenings, wheat starch and locust-bean gum respectively. The two other graphs (Fig. 8 and 9) represent tragacanth thickening and wheat starch thickening, respectively, mixed with a number of other thickenings.

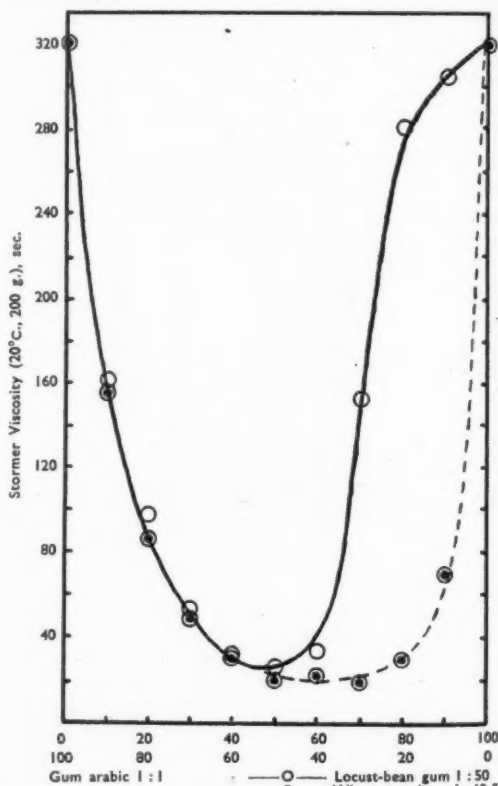


FIG. 7—Mixtures of Thickenings having Very High and Very Low Proportions of Dry Material respectively



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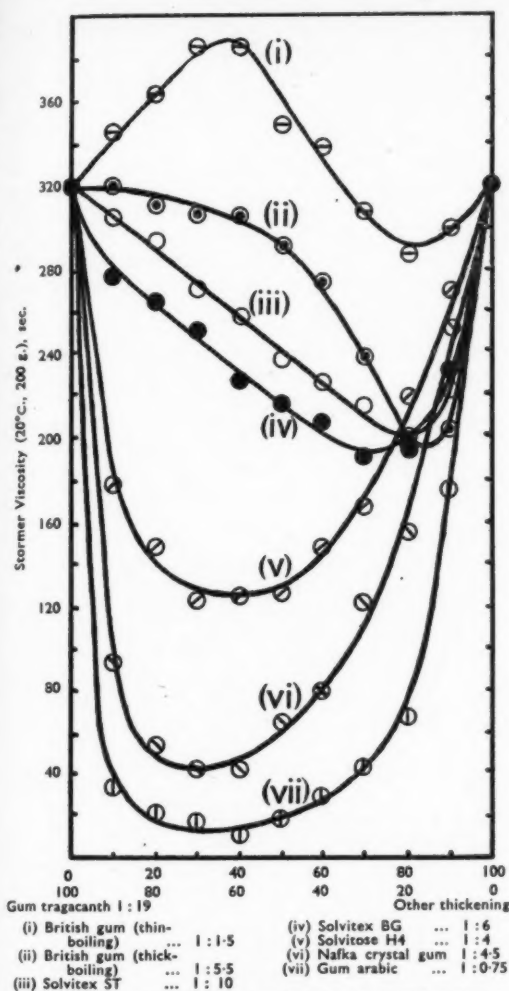


FIG. 8—Mixtures of Gum Tragacanth with Other Thickenings

In the first case (Fig. 7) the mixture taken was intentionally chosen so that a thickening of a gum of low thickening power, gum arabic, was mixed with a thickening of a gum of high thickening power. The very considerable drop in viscosity, shown by the almost perpendicular portion of the curve, indicates a very great mutual influence of the thickenings.

In the two other graphs (Fig. 8 and 9) results for a large number of mixtures have been plotted. There are only a very few mixtures which are not subject to a disadvantageous drop in viscosity. In connection with this it is of great importance that the thickening should mix well with starch, for, on account of its advantages, such as high colour value, especially in the case of cheap cloth, for which the disadvantages due to a poorer levelling power do not count so much, starch is indispensable. Whatever thickening may be used, mixing with starch is necessary and desirable, and this requirement is of prime importance. The curves clearly show that this is not the case with gums.

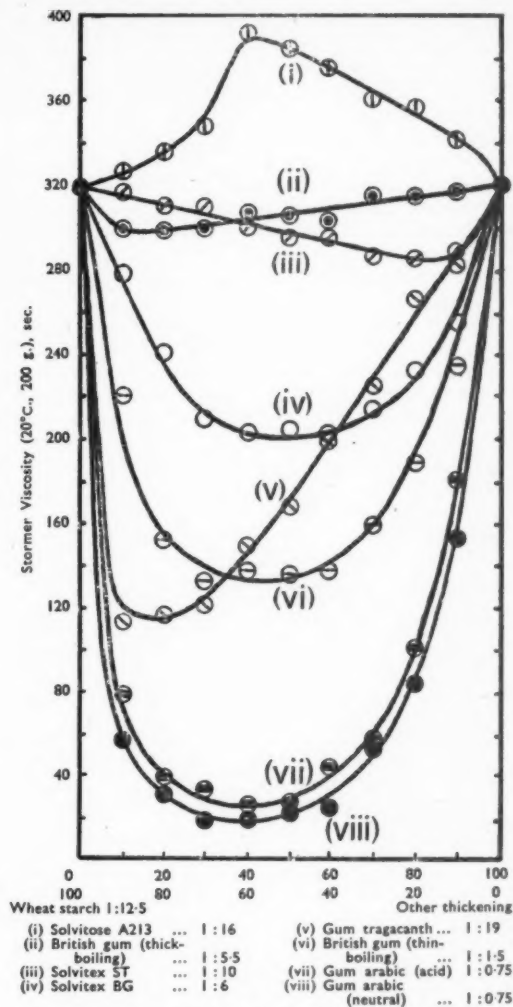


FIG. 9—Mixtures of Wheat Starch with Other Thickenings

Even wheat starch-tragacanth, which is so much used, shows a great drop in viscosity. It should be noted that the starch-tragacanth mixtures, to which the curve refers, were obtained by mixing in the cold, while in practice this thickening mixture is always made by boiling up the starch together with the dissolved tragacanth, and thereafter stirring it in the cold.

It is evident, however, that Solvitex ST and Solvitex A213 can very well be mixed with starch. On mixing Solvitex A213 (a variety of Solvitex C) with wheat starch, there is no drop in viscosity but, on the contrary, an increase in thickening power.

In seeking the cause of this great decrease in viscosity when thickenings are mixed, we should remember that thickenings are hydrophilic colloids. They swell and dissolve in water, the dispersed particles becoming charged and at the same time covered with a layer of water. Both the stability and the viscosity of the colloidal solutions depend on these two protective factors remaining intact. If

they are disturbed, a complete or partial precipitation may result. This is the case, for example, when an alcohol is added in increasing concentration to a hydrophilic colloid. The alcohol withdraws so much water from the colloid that the water shell is partly removed, and at a certain concentration the particles cannot remain dissolved. The same dehydration or withdrawal of water takes place, but less completely, when two thickenings are mixed. It is greatest when thickenings of low and high thickening powers are mixed. The particles of the one thickening partly withdraw the water molecules from the particles of the other thickening, to an intermediate stage between being dissolved in the colloidal state and precipitation. The particles of the two thickenings unite, and as the hydration layer still partly remains, precipitation is prevented. However, this phenomenon, termed *coacervation*, has an appreciable influence upon the viscosity. It is interesting in this connection to note that Rowson<sup>6</sup> found that the viscosities of mixtures of solutions of gum arabic and tragacanth, both of which are negatively charged, are lower than those of either of the component solutions.

Since coacervation occurs with most mixtures, it may be concluded from these observations that in general the mixing of thickenings should be avoided. However, further research in this field is required, as these phenomena can be influenced to a high degree by adding chemicals.

### 3. COLOUR YIELD, LEVELLING POWER, AND CHARACTER

These properties are considered together, as it will appear that they are connected with each other. A thickening agent that dissolves in the colloiddally dispersed state, e.g. gum arabic, has a better levelling power than a thickening agent consisting of a gel, i.e. of swollen particles, e.g. wheat starch. A colloidal solution contains many small particles, which moreover are well solvated. If the molecules of the colloiddally dispersed thickening agent are small macromolecules, then it possesses a low thickening power, e.g. gum senegal, gum arabic, British gum, etc. Such thickening agents assimilate the colouring matter better and it is also better dispersed by them than by starch, as they possess a higher power as protective colloids. On account of this the colouring matter is better, and especially in finer particles, transferred on to the cloth. Colloiddally dispersed thickenings also penetrate better the pores of the texture, as does the colouring matter when it is more finely divided. The simultaneous action of both these factors ensures that a printing colour with good levelling properties will penetrate well; i.e. its colour value will be low.

It is very surprising that the colour value is much greater when wheat starch is used, especially with vat dyes, than when other thickening agents are employed. It is known that the flocculating action of wheat starch upon suspensions of vat dyes is much greater than those of other thickening agents. In our opinion this is directly connected with the gel consistency of starch, owing to which the vat dye is much more coarsely dispersed in the

starch thickening. Moreover, starch consists for the greater part of large fragments of swollen granules. When in the course of printing the colouring paste is forced into the cloth under pressure, the cloth acts as a sieve, and prevents the coarse dye particles and the coarse thickening particles from passing through, so that these two substances together lie as a deposit on the surface of the cloth. It follows, therefore, that with such thickenings the colouring matter penetrates badly, but at the same time, owing to the bad dispersion, it possesses a poor levelling power. It appears from this that good levelling properties are inconsistent with high colour value. This holds good especially for the finer textures, which make high demands of the levelling power of the printing colour. In the case of coarse, loosely woven cotton fabrics, the poor levelling is not always obvious, but with closer textures, in which the sieve action is much finer, the fault of uneven prints shows itself much more clearly. Thus it is impossible to find a thickening agent which possesses both good levelling properties and a high colour value, especially on closely woven fabrics. This is demonstrated by the photomicrographs reproduced in Fig. 10-19.

Fig. 10 shows a potash printing colour containing Indanthren Blue RS (IG) paste and wheat starch thickening. Both the unevenly distributed dye agglomerates and the heterogeneous structure of the thickening can be seen. It is obvious that such a mixture cannot penetrate into the small pores of a fine-textured fabric, and thus cannot give a level print.

The dye is much more finely, and especially more evenly, distributed in Fig. 11, where a natural gum (gum arabic) has been used. The thickened mass is colloiddally dispersed and homogeneous. Such a mixture can penetrate into the finest texture and can give an even, unclouded print.

Fig. 12, obtained with Solvitose H4, shows a similar effect to Fig. 11.

A British gum thickening, though showing less homogeneity, also gives a similar picture (Fig. 13).

The same vat dye in the gum tragacanth thickening (Fig. 14) is still well distributed, though less finely divided. From experiments gum tragacanth appeared to have some flocculating effect upon a dye suspension, though far less than starch. A tragacanth solution is not completely dispersed colloiddally but is in a swollen condition, and its slight flocculating tendency and the coarser distribution of the dye are probably connected with this fact.

It is known in practice that a gum tragacanth thickening has a lower levelling power than an ordinary, colloiddally dispersed gum thickening, as is shown especially when they are applied on the finer qualities of cloth. Connected with this is the fact that the colour value with tragacanth is somewhat higher than with other gums.

The Solvitex BG printing colour (Fig. 15) gives a similar picture to gum tragacanth, but with a somewhat better homogeneity. This thickening agent is known to have tragacanth-like printing properties. Its levelling power is lower than that

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FIG. 4

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### Photomicrographs of Printing Colours made with Different Thickenings

(Indanthren Blue RS, C.I. 1106)

( $\times 600$ )

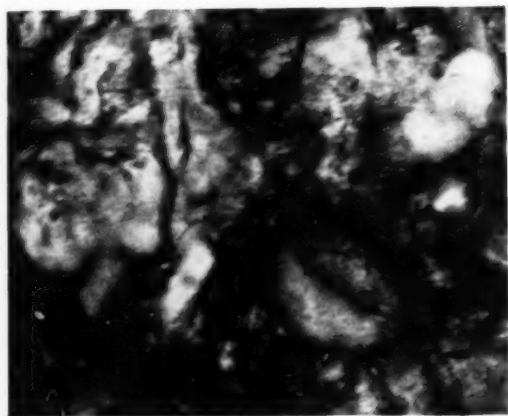


FIG. 10—Wheat Starch

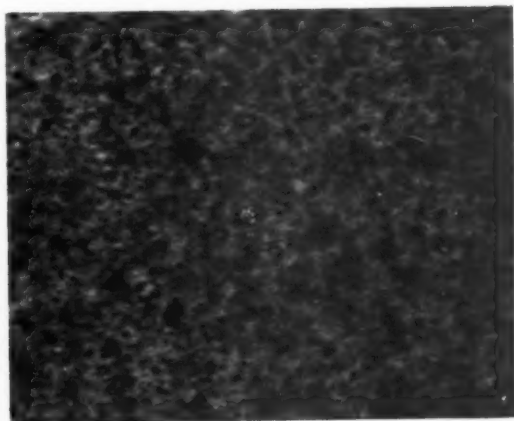


FIG. 11—Gum Arabic

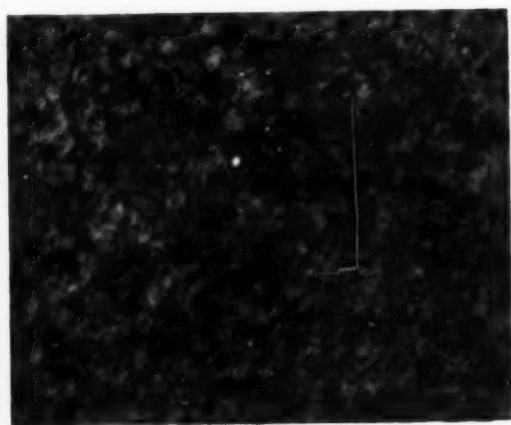


FIG. 12—Solvitose H4

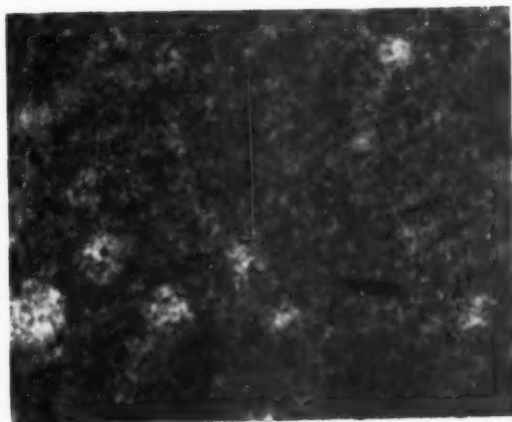


FIG. 13—British Gum

**Photomicrographs of Printing Colours made with Different Thickenings**

(Indanthren Blue RS, C.I. 1106)

( $\times 600$ )

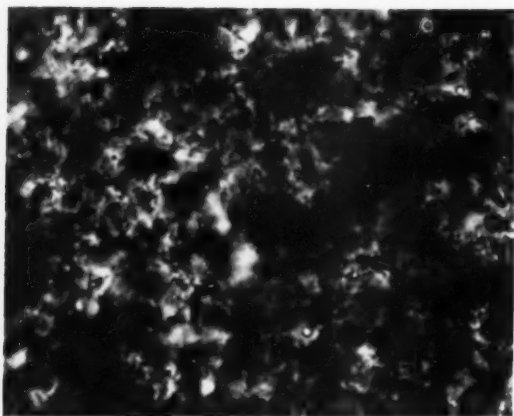


FIG. 14—Tragacanth

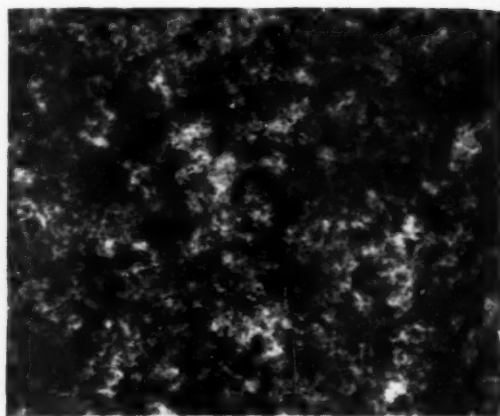


FIG. 15—Solvitex BG

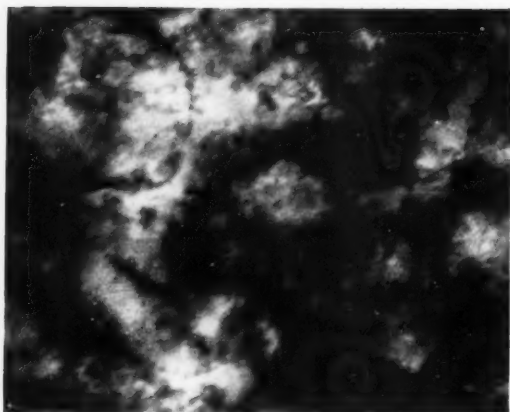


FIG. 16—Starch-Tragacanth

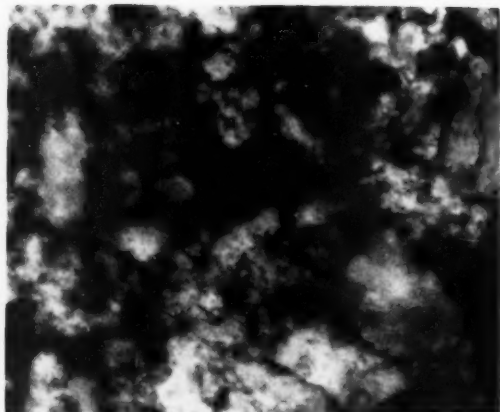


FIG. 17—Maize Starch



FIG. 18—Rice Starch

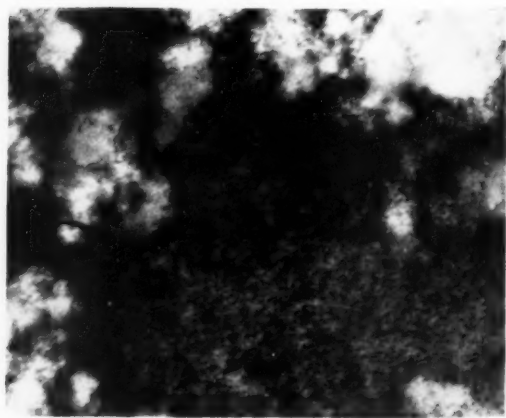


FIG. 19—Wheat Starch boiled for 4 hr. at  $> 2.5$  atm.



of gum arabic, but far better than that of starch, notwithstanding the fact that it is derived from the latter. But connected with this is the fact that in Solvitex BG printing paste the high colour value, so characteristic of starch, is lacking.

Fig. 16 shows a mixed starch-tragacanth thickening, and the picture also is strongly mixed, being between those for tragacanth and starch. The tragacanth performs the function of the levelling component, and the starch component provides for the high colour yield.

Fig. 17 and 18 show pastes with maize starch and rice starch. Both thickenings give a high colour yield and a heterogeneous distribution of the dye. It can be seen that the heterogeneity in all these printing pastes, which are made with natural starch, is almost the same.

Fig. 19 shows that the unevenness is not due to thorough boiling, and that it cannot be remedied thereby. The thickening employed consisted of wheat starch boiled for 4 hr. under a pressure of not less than 2.5 atm.

### Conclusion

In our opinion the immediate object of further study should be to simplify and improve the selection and number of thickeners in use. This in the long run may lead to standardisation, and therefore to better control, which will be in the interest of every textile print works.

W. A. SCHOLTEN'S CHEMISCHE FABRIEKEN N.V.  
FOXHOL  
HOLLAND

### References

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- <sup>2</sup> T. Posternak, *Helv. Chim. Acta*, **18**, 1351 (1935).
- <sup>3</sup> American Association of Textile Chemists and Colorists, Committee on Textile Printing Pastes, *Amer. Dyestuff Rep.*, **26**, 124, 437 (1937).
- <sup>4</sup> E. Knecht and J. B. Fothergill, *The Principles and Practice of Textile Printing* (London: Charles Griffin & Co. Ltd., 1936), p. 135.
- <sup>5</sup> Haller, *Melliand Textilber.*, **9**, 999-1000 (1928).
- <sup>6</sup> J. M. Rowson, *Quart. J. Pharm.*, **10**, 404 (1937).
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### Discussion

Dr. M. GEWING: Can Mr. Zonnenberg give a list of natural starches, as well as starch derivatives, in their order of rinsibility? I am chiefly interested in their use with vat dyes, but the order of rinsibility of the starches when used in a medium other than alkaline would also be interesting.

Mr. ZONNENBERG: Some comparative figures relating to the rinsibility of various starch products are given in Table III. The rinsibility was deter-

TABLE III

Products	Rinsibility (%)—		
	Neutral Thickening	Alkaline Thickening	Acid Thickening
Wheat starch ... ..	10	80	12
British gum (medium-boiling)...	65	90	50
British gum (thick-boiling) ...	49	81	44
Solvitose H type ... ..	85	95	74
Solvitose C type ... ..	95	97	55

mined by finishing pieces of cloth, weighed in advance, with the various thickenings adjusted to the same viscosity. These pieces were subsequently dried to constant weight, and then rinsed in cold running water for the same time.

Mr. D. A. REILLY: (1) In discussing the differences in printing behaviour between different starches, Mr. Zonnenberg has laid stress on the importance in this connection of the relative proportions of straight-chain amylose molecules and branched-chain amylopectin molecules. Referring to maize starch and potato starch, he quotes Samec in saying that the percentages of amylose are 53 and 22 respectively. This fits in well with the greater solution stability of potato starch. However, Schoch and his coworkers in America have investigated the amylose content of different starches by the butanol precipitation method, which appears to be very reliable, and they report that maize and potato starch both have the same amylose content of 22%. They suggest, with some support from end-group analyses, that the higher solution stability of potato starch is due to the fact that potato amylose has not in fact a strictly straight-chain molecule, but has a very small degree of branching, which would render it less liable to crystallise from solution. Has Mr. Zonnenberg any comments to make on this conflict of evidence?

(2) With reference to the suggestion that waxy maize starch has a very low amylose content, personal laboratory experience shows that on cooling, waxy maize starch pastes form little or no surface skin. Skin formation occurs with other starches, and is usually considered to be due to the presence of amylose.

Mr. ZONNENBERG: (1) It is well known that opinions on the proportions of amylose and amylopectin in the various kinds of starches are rather divergent, and it cannot be pretended that the figures given in the paper are absolutely right or give the latest results. They were primarily meant to show that there are in fact differences between the various kinds of starches.

To my knowledge Schoch's method<sup>7</sup> also gives differences between the percentages of amylose in potato starch and maize starch respectively, though these are smaller than originally quoted by Samec as shown in Table IV.

TABLE IV

	Amylose (%)
Maize starch ... ..	29
Potato starch ... ..	25
Tapioca starch ... ..	20

Whether the view that "the higher solution stability of potato starch is due to the fact that potato amylose has not a strictly straight-chain molecule, but a very small degree of branching" is correct I cannot confirm. In my opinion this is mainly caused by the fact that the amylopectin molecules in potato starch are more highly branched than in maize starch, and in addition have a higher molecular weight. Moreover, the amylose molecules of potato starch possess a higher molecular weight than the amylose molecules of corn starch and hence the former starch is less

liable to crystallise, which results also in the greater stability of a potato starch solution.

(2) I agree with Mr. Reilly's opinion that the absence of skin formation in the case of waxy maize starch pastes is due to the fact that waxy maize starch is substantially pure amylopectin. The Solvitoses also do not show skin formation, as etherification makes the amylose also branched, resulting in the complete or almost complete disappearance of the power of crystallisation.

Mr. H. A. TURNER: In dealing with the relation of thickener to colour value, Mr. Zonnenberg has quite rightly, in my opinion, paid considerable attention to the mechanical factors, viz. the dispersion of the dye and the penetration of the paste into the fabric under the actual conditions of making the impression. This is probably of special importance when—as in vat styles—the dye is presented to the cloth in an insoluble form. I would like to call attention to another aspect, probably of greatest importance with soluble dyes, viz. the possibility that colour value can be determined as the difference between the affinity of the dye for the thickener and the competing affinity of the dye for the fibre. Here some of the products that Mr. Zonnenberg has mentioned may have a special fundamental interest. In studying the diffusion of a pure direct dye from a film of thickener to a film of cellulose during steaming, Mr. Reilly and I have found that the presence of ionic groups in the thickener can exercise a considerable influence on the amount of dye transferred; e.g. under conditions which give a transfer of 60–70% of the total dye with neutral starch, there is 100% transfer when sodium alginate is the thickener. In simple words, it can be considered that the charged carboxyl ionic groups in the alginate repel the negative dye ions more than the natural negative surface charge of cellulose and therefore force the dye into the cellulose. There seem, therefore, to be very strong probabilities that the substituted starch ethers that Mr. Zonnenberg has described will do the same. If the carboxyl and the sulpho groups are present as the salts and are fully ionised, they could exert an analogous action to the carboxyl groups of the alginate. If the sulpho group is present in appreciable proportions it should do this with especial ease, not merely at pH 7 but at lower pH values, and it may

cause not merely complete but also rapid exhaustion. We should be interested to hear from Mr. Zonnenberg whether he has met with distinctive behaviour corresponding to the effect described when these acidic ether products are used with either direct or acid dyes in printing.

Mr. ZONNENBERG: We have not yet fully examined the matter, but we expect the Solvitoses to behave in the manner suggested.

Mr. J. GRUSCHKA: The lecturer stated that the fall in viscosity accompanying the mixing of certain thickeners of similar viscosity can be attributed *inter alia* to a difference in electrical charge on the two thickeners. When he was referring to "difference" in electrical charge, did he mean to imply that the thickeners can be oppositely charged? If so, will he give us an instance of a printing thickener carrying a positive charge?

Mr. ZONNENBERG: As was stated in the lecture, the fall in viscosity accompanying the mixing of certain thickenings is in the first place due to the destruction of the water shells enclosing the particles of one colloid by the particles of the other, as a result of a difference in potential between the different colloidal particles.

In case of thickenings having opposite charges, the phenomenon will no doubt be more marked. The most usual thickenings, such as starch, starch derivatives, tragacanth, and gum arabic, all possess a negative charge (albumen, gelatin, and casein are positive at pH values below their isoelectric points), and when two of the said thickenings are mixed, the drop in viscosity will be due mainly to dehydration.

Mr. R. THORNTON: Has Mr. Zonnenberg or his firm had any experience of the change of viscosity normally associated with starch printing thickenings in the presence of unstable diazonium compounds? The normal finding is an excessive drop in viscosity, but occasionally an increase is observed, probably due to aeration by gaseous by-products.

Mr. ZONNENBERG: We have indeed found an excessive drop in viscosity with certain unstable diazonium compounds, and this is most marked with diazotised *p*-nitroaniline. This we ascribe to a breakdown of the starch by oxidation. By a special etherification of starch we have succeeded in preventing the drop in viscosity.

## COMMUNICATION

## The Relation between the Rate of Formation of the Chromium Complexes of a Dye and its Value in the Metachrome Process

E. RACE

A study has been made of the rates of formation and the nature of the chromium complexes of selected dyes in order to ascertain whether or not a relationship exists between the rate of complex formation and the suitability of a dye for application by the metachrome process. The results indicate that, in the case of azosalicylic acid compounds containing a sulpho group, the dyes are unsuitable for use in the metachrome process probably because of co-ordination of chromium with the sulpho group instead of, or as well as, chelation of chromium with the salicylic acid group. The examination of the rates of formation of the chromium complexes of a series of *oo'*-dihydroxyazo compounds of diminishing value as metachrome dyes has revealed that the greater the rate of chromium-dye complex formation the more suitable is the dye for application by the metachrome process. The results suggest that both substantivity and rate of complex formation play important rôles in the determination of the value of a metachrome dye, and that both of these factors should be as high as possible, consistent with solubility.

The experimental data demonstrate that, in the case of the series of *oo'*-dihydroxyazo dyes employed, the final product of reaction of dye and chromium salt is the primary complex, in which one molecule of dye is associated with one atom of chromium. This product is formed via the chromium salt of the dye and a complex in which three molecules of the dye are associated with one atom of chromium. The analyses have not disclosed whether conversion of the 3 : 1 complex occurs directly to the 1 : 1 complex or whether the 2 : 1 acidic complex is formed as an intermediate product.

Whether or not a chrome dye is suitable for application by the metachrome process depends on a number of considerations; thus, a good metachrome dye fulfils the following conditions—

- It exhausts well from the metachrome dyebath in normal dyeing times.
- It does not precipitate either in the dyebath or on the surface of the fibre.
- It produces dyeings of fastness to washing, rubbing, and light equal or superior to those produced by the afterchrome or chrome mordant processes.
- It forms a true dye-chromium complex on the fibre.

When these criteria are applied to the empirical assessment of the suitabilities of lake-forming dyes for application by the metachrome process, it is observed that the dyes which are of greatest value are those which possess high substantivity for wool from an acid dyebath. Since the rate at which wool combines with chromium in a boiling metachrome dyebath is independent of the presence of dye<sup>1</sup>, it is by no means clear why substantivity of the dye should play so important a rôle in metachrome dyeing. Indeed, it might be expected that any dye possessing chelating groups would prove, in practice, to be a satisfactory metachrome dye providing (i) that complex formation is not so rapid as to result in insoluble lake formation in the dyebath, and (ii) that complex formation is not so slow as to extend the time of dyeing beyond the limits of practicability. It appears not improbable that substantivity is an essential feature of existing metachrome dyes only because the rates of formation of their chromium complexes are low. Alternatively, it is possible that the substantivity on wool of a dye possessing chelating groups and the rate of formation of its chromium complex are interrelated; i.e. a dye exhibiting high substantivity (and therefore, in general, a relatively low solubility) is also one which has a high rate of complex formation. If such be the case, it would seem that an increase in either the number or the power of the solubilising groups results in a

corresponding decrease in the chelating power of the lake-forming groups, and the rate at which the lake is formed, rather than, or as well as, the substantivity of the dye, plays an important rôle in determining whether or not the dye will be suitable for use in the metachrome process. Whether or not this is so has been examined by studying the rates of formation of the chromium complexes of selected dyes, the suitability for use in the metachrome process of which had been predetermined experimentally in accordance with the four criteria (a)–(d) above.

The principle of the method is as follows—Known amounts of a highly purified dye and chromic sulphate in aqueous medium were allowed to interact at various temperatures for a specified time or at a specified temperature for various times, the rate of formation and nature of the dye-chromium complex being followed by analysis of the solid product and determination of precipitable and non-precipitable chromium in the solution.

In the first instance, the investigation was confined to three dyes of comparatively simple structure, viz.—

- Aniline- $\rightarrow$ salicylic acid
- Sulphanilic acid- $\rightarrow$ salicylic acid
- Metanilic acid- $\rightarrow$ salicylic acid

this series diminishing from (a) to (c) in value as metachrome dyes.

The dyes were purified by successive recrystallisations from water, followed by repeated extractions with ethyl alcohol, and gave the results shown in Table I for purity by titration with titanous sulphate and determination of sodium content. All three dyes were monosodium salts.

The chromic sulphate used was the pure octadecahydrate  $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , the whole of the chromium being precipitable from a freshly prepared solution.

TABLE I

Dye	Purity (%)	
	By Titanous Titration	By Sodium Determination
Aniline- $\rightarrow$ salicylic acid...	97.6	98.3
Sulphanilic acid- $\rightarrow$ salicylic acid	98.6	97.3
Metanilic acid- $\rightarrow$ salicylic acid	98.7	97.2

One millimole of each dye in 100 ml. of water and 1.5 millimoles of chromium sulphate (equivalent to 3 milligram-atoms of chromium) were allowed to interact at 36°C. for 30 min., after which chromium was precipitated from the reaction mixture with excess ammonia, precipitable and non-precipitable chromium being estimated by titration with ferrous ammonium sulphate after oxidation with perchloric, nitric, and sulphuric acids. The procedure was repeated at 47°C.

Interpretation of the results was, however, found impossible, and further experiments showed that the method possessed the following three major defects, any or all of which could account for results not capable of a simple interpretation—

(a) Addition of the chromium sulphate solution to the sodium salt of phenylazosalicylic acid produced an immediate precipitate, representing 90% of the initial amount of dye, which, after reaction for 30 min. at 36°C., was composed of 98% free dye acid and 2% dye-chromium complex. In the case of the other two dyes, no precipitation occurred at either temperature. It was found that tenfold dilution of the reaction mixture prevented precipitation of the free dye acid of phenylazosalicylic acid.

(b) Since both dyes containing a sulpho group were monosodium salts, the pH values of their solutions were much lower than that of a solution of phenylazosalicylic acid. The actual pH values of the solutions, before the addition of chromium sulphate, were as follows—

Aniline→salicylic acid...	5.43
Sulphanilic acid→salicylic acid	2.52
Metanilic acid→salicylic acid	2.53

Conversion of the two dyes containing sulpho groups into disodium salts resulted in their solutions having the following pH values—

Sulphanilic acid→salicylic acid	5.77
Metanilic acid→salicylic acid	5.90

By accurately controlled additions of sodium hydroxide, it was shown that the variations in pH values were not due to small inaccuracies in amounts of sodium hydroxide added, but to differences in  $pK$  of the carboxyl groups of the three dyes. In any case, the addition of chromium sulphate to the solutions smoothed out the differences, and gave the following pH values—

Chromic sulphate alone...	3.41
Aniline→salicylic acid (monosodium salt) + chromic sulphate	3.45
Sulphanilic acid→salicylic acid (disodium salt) + chromic sulphate	3.45
Metanilic acid→salicylic acid (disodium salt) + chromic sulphate	3.46

(c) Addition of a comparatively large excess of ammonia to the chromium sulphate solutions resulted in the production of soluble chromamines, thereby giving erroneous results for the proportion of precipitable chromium. This was overcome by using an amount of ammonia only slightly in excess of the stoichiometric amount required for the precipitation of the whole of the chromium present in the solution.

As a result of a number of experiments, the following procedure was finally adopted—

To 0.25 millimole of dye in 200 ml. of water at 47°C. was added 0.375 millimole of chromium

sulphate in 10 ml. of water at 47°C., the chromium sulphate being washed into the dye solution with a further  $3 \times 3$  ml. of water at 47°C. The reaction solution was maintained at 47°C. for a specified time, after which the solution was immediately cooled to 0°C., any solid product being quickly filtered off and washed, and to the filtrate at 0°C. were added 1 g. of ammonium chloride and 1 ml. of 17.5% ammonia. In the case both of the dye aniline→salicylic acid and of the chromium sulphate control, the chromic hydroxide could readily be filtered off and washed on the filter, but in the case both of sulphanilic acid→salicylic acid and of metanilic acid→salicylic acid, the much smaller amount of precipitate was too colloidal to be filtered off, and centrifuging at 4000 r.p.m. for 15 min. was necessary for both separating and washing the chromium hydroxide.

Using this technique, the results given in Table II were obtained.

TABLE II

Time of Reaction (hr.)	Dye	Initial pH	Final pH	Precipitable Chromium	Non-precipitable Chromium	Chromium in Solid Product
				(% of total initial chromium)		
1	Chromium sulphate control	3.41	3.46	100.6	0.12	—
	Aniline→salicylic acid	3.45	3.46	98.14	0.57	0.30
	Sulphanilic acid→salicylic acid	3.45	3.62	56.40	43.52	—
	Metanilic acid→salicylic acid	3.46	3.50	74.23	25.86	—
2	Chromium sulphate control	3.41	3.46	100.2	0.12	—
	Aniline→salicylic acid	3.45	3.47	97.40	0.97	1.31
	Sulphanilic acid→salicylic acid	3.45	3.69	24.82	75.51	—
	Metanilic acid→salicylic acid	3.46	3.62	34.14	65.94	—
4	Chromium sulphate control	—	—	99.82	0.16	—
	Aniline→salicylic acid	—	—	96.24	1.93	1.90
	Sulphanilic acid→salicylic acid	—	—	16.50	84.05	—
	Metanilic acid→salicylic acid	—	—	21.71	78.16	—
8	Chromium sulphate control	—	—	99.90	0.10	—
	Aniline→salicylic acid	—	—	94.22	3.71	2.33
	Sulphanilic acid→salicylic acid	—	—	13.18	87.44	—
	Metanilic acid→salicylic acid	—	—	18.37	82.02	—
16	Chromium sulphate control	3.41	3.07	100.2	0.12	—
	Aniline→salicylic acid	3.45	3.03	92.29	5.89	2.57
	Sulphanilic acid→salicylic acid	3.45	2.90	11.77	89.10	—
	Metanilic acid→salicylic acid	3.46	2.93	16.83	83.59	—

It was only in the case of the dye aniline→salicylic acid that small amounts of solid reaction products were formed. The weights of product deposited and the ratios of dye to chromium in them are given in Table III.

TABLE III

Time of Reaction (hr.)	Wt. of Solid Product (mg.)	Approx. % of Total Dye converted into Solid Product	Approx. Dye : Cr Mol. Ratio in Solid Product
1	6.0	9.3	10.0
2	10.5	15.7	4.0
4	14.6	21.3	3.8
8	17.0	25.3	3.6
16	18.3	27.2	3.5

The fact that the molecular ratio of dye to chromium in the insoluble product decreases as the time of reaction increases indicates that a pure insoluble complex is not being produced. Because of the small amounts of insoluble product, undue emphasis must not be laid on the calculated ratio



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Table II

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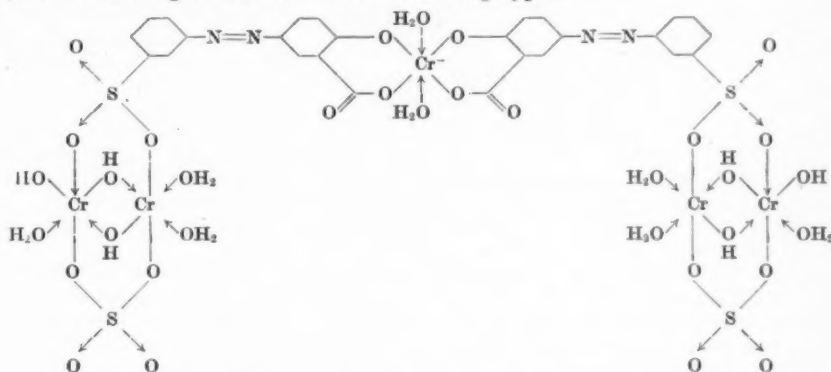
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of dye to chromium; indeed, it is not improbable that this deposit, which was deep reddish brown, is a decomposition product of the dye which either combines with or occludes a small amount of chromium. This belief is supported by the fact that scum formation in the metachrome dyebath is greater in the case of aniline→salicylic acid than in the case of either sulphanilic acid→salicylic acid or metanilic acid→salicylic acid, even though the first-named is a much superior metachrome dye. Against this belief, however, is the fact that the rate of formation of solid product is far from constant, whereas it might be expected that, at constant temperature, the rate of decomposition of dye would be itself constant. It is possible, of course, that the insoluble product is a mixture of true complex and decomposition product.

Whatever the nature of the deposit in the case of the dye aniline→salicylic acid, it is clear that the rates of chelation and/or co-ordination of chromium in the case of sulphanilic acid→salicylic acid and metanilic acid→salicylic acid are very much greater than in the case of aniline→salicylic acid. This is emphasised in Table IV, in which the amounts of non-precipitable (i.e. chelated and/or co-ordinated) chromium are recalculated as atoms of chromium per molecule of dye. In the case of aniline→salicylic acid, two values are given in each

appear that the main factor in the superiority of aniline→salicylic acid is its slowness of complex formation in the dyebath.

Unless the dye ion catalyses co-ordination of chromium sulphate independently of dye-chromium complex formation, it would seem from the data that complex formation in the case of the two dyes containing sulpho groups is resulting in a product in which either two molecules of dye are associated with five atoms of chromium or one molecule of dye is associated with three atoms of chromium. It is difficult to formulate a structure entailing chelation of three atoms of chromium with single *o*-carboxy-hydroxy groups without stipulating the presence of either -Cr-O-Cr- linkages or an abundance of co-ordinated water molecules. A chromium salt of the sulphonic acid would, if soluble, be ionised, and would therefore yield precipitable chromium. The most reasonable explanation appears to be that chromium co-ordinates with the sulpho group of the dye, possibly forming a sulphato-sulphonatochromium complex. In order to satisfy the analytical data, it appears necessary to assume that co-ordination of chromium with the hydroxyl and carboxyl groups of the salicylic acid component of the dye also occurs. Such a complex might have a structure of the following type—



case, one (not in parentheses) in which it is assumed that the insoluble product is a decomposition product of the dye which has absorbed chromium which otherwise would have remained precipitable, and the other (in parentheses) in which it is assumed that the solid product is dye-chromium complex and in which the chromium must, therefore, be regarded as non-precipitable.

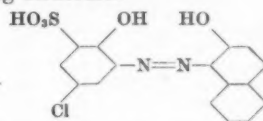
TABLE IV

Dye	Non-precipitable Cr : Dye Ratio after—				
Time of reaction, hr. ...	1	2	4	8	16
Aniline→salicylic acid...	0.018 (0.027)	0.030 (0.071)	0.060 (0.119)	0.115 (0.188)	0.183 (0.263)
Sulphanilic acid→ salicylic acid ...	1.36	2.35	2.62	2.72	2.77
Metanilic acid→ salicylic acid ...	0.80	2.05	2.43	2.55	2.60

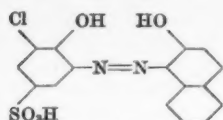
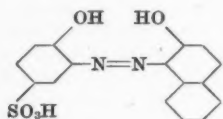
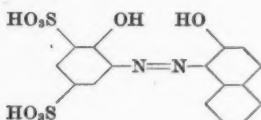
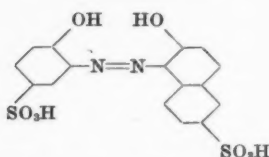
Thus, there is a striking difference between the rate of chelation and/or co-ordination of chromium in the presence of aniline→salicylic acid and the rate in the presence of either of the other two dyes. If this difference is due to differences in rates of formation of dye-chromium complex, it would

Because of its size and deficiency in acidic groups, a complex of this type would exhibit less affinity for the fibre than either the parent dye or a complex containing free sulphonyl groups.

The above results tend to emphasise a fact which has been apparent in previous investigations<sup>2</sup> concerned with the elucidation of dye-chromium complexes formed on wool, viz. that the reaction between the azosalicylic acids and chromium salts is not one which is capable of a simple interpretation. Attention was, therefore, directed to a series of *oo'*-dihydroxyazo dyes, the suitability of which for use in the metachrome process had been predetermined as before. The dyes employed had the following structures—



(1) 4-Chloro-2-aminophenol-6-sulphonic acid→β-Naphthol (monosodium salt)

(2) 6-Chloro-2-aminophenol-4-sulphonic acid  $\rightarrow$   $\beta$ -Naphthol (monosodium salt)(3) 2-Aminophenol-4-sulphonic acid  $\rightarrow$   $\beta$ -Naphthol (monosodium salt)(4) 2-Aminophenol-4:6-disulphonic acid  $\rightarrow$   $\beta$ -Naphthol (disodium salt)(5) 2-Aminophenol-4-sulphonic acid  $\rightarrow$  2-Naphthol-6-sulphonic acid (disodium salt)

As tested by the criteria outlined on p. 141, this series diminishes from (1) to (5) in value as meta-chrome dyes.

Dyes (1) and (3) were purified by successive recrystallisations from water, followed by repeated extractions with ethyl alcohol; dye (2) was purified by successive recrystallisations from water containing 10% ethyl alcohol, followed by repeated extractions with ethyl alcohol; and dyes (4) and (5) were purified by the method which Robinson and Mills<sup>3</sup> applied to direct cotton dyes, involving successive dissolutions of the dye in minimal quantities of water, the dye being salted out each time with pure sodium acetate; the residual sodium acetate was removed by repeated extractions with absolute alcohol, and the dye was finally dissolved in water, the solution being filtered and the filtrate carefully evaporated to dryness. All the dyes had purities greater than 98.5%.

The method of following the rates of formation of the dye-chromium complexes was similar to that described in the case of the azosalicyclic acid compounds; because of the low solubilities of dyes (1) and (2), however, working concentrations were necessarily low. The pure sodium salt of the dye (0.25 millimole) was dissolved in 1 litre of water at 50°C., and 0.5532 g. of chromium sulphate (containing 84.8 mg. of chromium, equivalent to 1.627 mg.-atom, the chromium sulphate approximating to  $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ ), freshly dissolved in 10 ml. of water at 50°C., was added, the chromium sulphate being washed into the dye solution with a further  $3 \times 3.3$  ml. of water. The reaction was allowed to continue at 50°C. for a specified time, after which the reaction mixture was cooled rapidly to 0°C. in a freezing mixture, the solid product being filtered off as quickly as possible into a tared sintered glass filter, washed free from solution with minimal quantities of ice-cold water, and dried to constant weight at 105°C. The chromium content of the solid was estimated by oxidation with perchloric, nitric, and sulphuric acids, followed by microtitration of the chromic acid at 0°C. with 0.01 N. ferrous ammonium sulphate. To the filtrate and washings, still maintained at 0°C., were added 1 g. of ammonium chloride and 3 ml. of 16% ammonia. The precipitate of chromium hydroxide was allowed to settle at 0°C. overnight and was then filtered without suction through a fine ashless filter-paper, the precipitate being washed completely free from dye. Chromium was estimated in the precipitate by ashing, oxidising with the perchloric acid mixture, and titrating with 0.1 N. ferrous ammonium sulphate; and in the filtrate by evaporating to dryness, oxidising, and microtitrating at 0°C. with 0.01 N. ferrous ammonium sulphate.

The results of the estimations are given below.

#### 1. SOLID PRODUCTS

The weights, chromium contents, and molecular weights with respect to chromium of the solid products formed during the reactions are given in Table V.

At the necessarily low concentration employed throughout the complete series, it was only in the cases of dyes (1)–(3) that the chromium complexes formed were of solubility low enough to yield a solid product. For each reaction time, the amount of this solid product is greatest in the case of dye (1) and least in the case of (3). The solubilities of the chromium complexes appear, therefore, to follow the solubilities of their parent dyes, since both the sodium salt and the free acid of (1) are respectively less soluble than, and the sodium

TABLE V

Dye ... Time of Reaction (hr.)	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	Wt. of Solid Product (mg.)					Chromium Content of Solid Product (mg.)					Wt. of Complex containing 1 Cr				
0.5	75.1	56.4	Nil	Nil	Nil	3.28	2.66	—	—	—	1191	1180	—	—	—
1	76.6	61.7	Nil	Nil	Nil	3.59	2.90	—	—	—	1109	1106	—	—	—
2	79.3	62.3	53.6	Nil	Nil	3.99	3.09	2.71	—	—	1034	1048	1029	—	—
4	82.6	63.9	57.1	Nil	Nil	4.55	3.43	3.18	—	—	944.1	968.5	932.8	—	—
8	85.0	66.5	61.3	Nil	Nil	5.62	4.11	3.74	—	—	805.1	841.5	853.0	—	—
16	92.2	71.2	64.4	Nil	Nil	7.32	5.26	4.49	—	—	654.6	703.6	746.2	—	—
42	100.0	84.4	65.7	Nil	Nil	9.91	7.01	4.75	—	—	524.6	626.0	718.7	—	—
96	105.2	96.6	65.9	Nil	Nil	11.15	8.60	4.95	—	—	490.7	583.9	693.6	—	—

TABLE VI

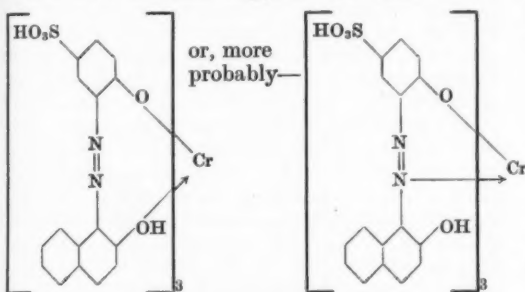
Dye	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Time of Reaction (hr.)	Wt. of Product used in Estimation (mg.)			Wt. of Ash (mg.)			Chromium Content of Ash (mg.)			Cr <sub>2</sub> O <sub>3</sub> in Ash (%)			Mol. Wt. of Product calculated from Wt. of Ash		
0.5	125.4	100.4	—	8.0	6.7	—	5.44	4.41	—	99.4	97.4	—	1191	1133	—
4	146.6	117.4	100.2	12.0	9.2	8.3	8.26	6.28	5.58	100.6	98.4	93.3	930	970	918
16	163.5	129.0	106.5	19.1	14.0	11.0	12.93	9.72	7.44	99.4	101.5	93.8	651	700	736
96	186.8	163.1	105.8	23.4	22.4	11.8	19.20	15.10	7.95	98.8	93.6	93.5	500	571	681

salt and the free acid of (3) are respectively more soluble than, the sodium salt and the free acid of (2).

That none of the solid products was a sodium salt was proved by further analysis of the deposits formed after 0.5, 4, 16, and 96 hr. Double quantities of reactants were used, and, in each case, the major portion of the solid product was ashed at incipient red heat, the green residue being weighed, oxidised to chromic acid, and microtitrated with standard ferrous ammonium sulphate. The results are given in Table VI.

Thus, the products formed are chromium complexes of the free dye acids.

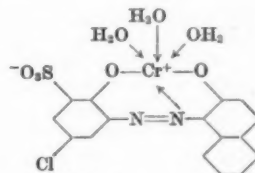
In the case of the three dyes which yield solid products, the initial deposit (Table V) is one in which one atom of chromium is associated with three molecules of dye. Both the chromium salt and a 3:1 chelated complex, e.g. either—



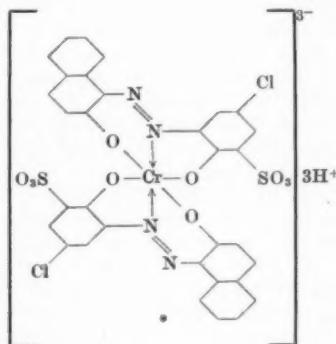
have in the cases of dyes (1) and (2) molecular weights of 1184.5, and in the case of (3) a molecular weight of 1081. The experiments were repeated for 0.5, 1, 2, 4, 8, 16, 42, and 96 hr. in the case of dyes (1) and (2), and for 2, 4, 8, 16, 42, and 96 hr. in the case of (3). The solid products were isolated, a weighed amount of each being shaken with 3 litres of water, and to the partial solutions 3 ml. of 16% ammonia was added. After having stood with frequent shaking for 24 hr., the products formed during reaction times of 0.5, 1, 2, and 4 hr. were completely dissolved, but only partial solution occurred of products formed after reaction times of 8, 16, 42, and 96 hr. The ammoniacal solutions of products formed up to 4 hr. were filtered without suction through No. 40 Whatman filter-papers, any chromium hydroxide on the filter-papers being washed free from dye solution and estimated by ashing, oxidation, and microtitration. In the case of the product formed from (1) after 0.5 hr. reaction, 29.7% of the chromium was precipitable with ammonia, whereas after 1, 2, or 4 hr. reaction, none of the chromium in the product was precipitable. On the other hand, in the case of the product formed from (2), after 0.5 hr. 53.1%, and after 1 hr. 11.4%, of the chromium was precipitable with

ammonia, but the products formed after 2 and 4 hr. reaction from both this dye and (3) yielded no chromium hydroxide from their ammoniacal solutions.

It is apparent, therefore, that the initial reaction is the conversion of the dye into its chromium salt, which, under the conditions of the experiments, is partly insoluble in the cases of dyes (1) and (2), and wholly soluble in the cases of dyes (3), (4), and (5). The chromium salt is in turn relatively rapidly converted into a complex in which one atom of chromium is associated with three molecules of dye. The final product of reaction, after about 96 hr. in the case of (1), after a longer period in the case of (2), and after a still longer period in the case of (3), is one in which one atom of chromium is associated with one molecule of dye. The molecular weight with respect to chromium of the complex formed from (1) after reaction for 96 hr. suggests that this complex has the following structure (mol. wt. 481.5)—



This complex might be formed either directly from the 3:1 complex\* or through the acidic 2:1 complex<sup>4,5</sup>—



Unfortunately, it was found that the differences in solubility in water of the various complexes formed were not great enough to allow separation of any complex in a pure state. Therefore, in calculating the empirical compositions of the solid reaction products, two assumptions have been made—(a) that the reaction proceeds from the 3:1 complex to the 1:1 complex via the 2:1 complex,

\* By the 3:1, 2:1, and 1:1 complexes are meant those chelated compounds in which 3, 2, and 1 molecule of dye, respectively, are associated with one atom of chromium.

TABLE VII

Dye ... Time of Reaction (hr.)	1	2	3	1	2	3	1	2	3	1	2	3
	Chromium Salt (%)			3 : 1 Complex (%)			2 : 1 Complex (%)			1 : 1 Complex (%)		
0.5	29.7	53.1	—	70.3	46.9	—	Nil	Nil	—	Nil	Nil	—
1	Nil	11.4	—	80.0	67.9	—	20.0	20.7	—	Nil	Nil	—
2	Nil	Nil	Nil	60.2	63.9	84.9	39.8	36.1	15.1	Nil	Nil	Nil
4	Nil	Nil	Nil	36.5	42.9	56.9	63.5	57.1	43.1	Nil	Nil	Nil
8	Nil	Nil	Nil	Nil	9.4	33.7	99.7	90.6	66.3	0.3	Nil	Nil
16	Nil	Nil	Nil	Nil	Nil	2.6	53.0	68.4	97.4	47.0	31.6	Nil
42	Nil	Nil	Nil	Nil	Nil	Nil	13.3	44.5	93.7	86.7	55.5	6.3
96	Nil	Nil	Nil	Nil	Nil	Nil	3.1	31.5	85.0	96.9	68.5	15.0

and (b) that only two products are present in the reaction mixture at a given time. (Assumption (a) may be correct, but assumption (b) can at most give only an indication of the rate of conversion from one complex to another.) Table VII gives the empirical compositions of the solid products based on these assumptions.

Two conclusions arise from these data—

(i) that in the three cases in which solids are deposited, the final reaction product is a 1 : 1 complex obtained from the dye via the chromium salt and the 3 : 1 complex; and

(ii) that dye (1) completes this series of reactions more rapidly than (2), which, in turn, completes the series more rapidly than (3).

## 2. CHROMIUM SALT OF DYE AND DYE-CHROMIUM COMPLEX IN SOLUTION

The fact that no chromium hydroxide is precipitated from weakly ammoniacal solutions of solid complex products which do not contain chromium salt of dye proves that the complexes in solution are stable in dilute ammonia, at any rate in the case of the three dyes which yield solid products. Consequently, in precipitating chromium from the reaction solutions from which deposited products have been removed, it is justifiable to assume in the case of these three dyes that any non-precipitable chromium is co-ordinated with dye in solution, particularly in view of the further fact that control experiments with chromium sulphate alone showed that, even after 96 hr. at 50°C., less than 0.15% of the chromium was non-precipitable with ammonia. By inference, it appears to be a reasonable assumption that the same is true of those dyes (No. 4 and 5) with which no solid products are formed.

In the case of dyes (1)–(3), in order to calculate from their chromium contents the amounts of dye-chromium complex remaining in solution after removal of solid products and precipitable chromium, it is necessary to assume that the composition of complex in solution is identical with

that of the solid product. The results based on this assumption are probably reasonably accurate, since the solubilities of the various complexes formed are relatively low and do not differ widely. Furthermore, a balance sheet of the percentages of the initial amount of dye converted into chromium salt and/or complex (see Table IX), especially in the case of (1), shows values approximating to 100%. However, since in reactions of the type in which continual conversion from one complex to another is taking place it is essential to halt the reaction, or reduce its rate to negligible proportions, at the end of the specified reaction time, it was impossible in the case of the two dyes yielding no solid dye-chromium products to ascertain the nature of the intermediate complexes formed in solution. Thus, in the case of (1), (2), and (for reaction times greater than 2 hr.) (3), Table VIII gives the chromium contents and weights of chromium salt of dye and/or dye-chromium complex remaining in solution after the removal of solid products, the weights being calculated from the molecular weights of the corresponding solid products. In the case of the two remaining dyes, which yielded no products out of solution, only the chromium contents, and not the weights, of dye-chromium complexes in solution can be computed from the analytical data. Whether or not reactants and products remain in solution, the fully ionised chromium salt of the dye is, in effect, formed instantaneously on the addition of chromium sulphate solution to dye solution.

The data in Table VIII illustrate the fact that, in the cases of dyes (4) and (5), with which no solid products are formed, dye-chromium complex formation is, nevertheless, occurring, although the products remain in solution.

## 3. BALANCE SHEETS

(a) DYE—It is, of course, only in the cases of those dyes which yield solid products that the proportion of dye converted into complex can be computed, and, even here, the calculations are

TABLE VIII

Dye ... Time of Reaction (hr.)	1	2	1	2	1	2	3	4	5	1	2	3
	Chromium Salt of Dye in Solution*		Weight (mg.)		Dye-Chromium Complex in Solution							
	Chromium Content (mg.)				Chromium Content (mg.)					Weight (mg.)†		
0.5	0.80	0.81	6.7	18.4	0.70	0.72	1.14	1.04	0.80	16.0	16.3	—
1	Nil	0.14	Nil	3.2	1.11	1.45	2.22	1.05	1.21	23.5	29.8	—
2	Nil	Nil	Nil	Nil	0.99	1.54	1.11	2.73	1.08	19.8	31.1	22.0
4	Nil	Nil	Nil	Nil	0.99	1.75	1.33	3.74	2.03	17.9	32.6	23.9
8	Nil	Nil	Nil	Nil	1.19	2.06	1.80	4.60	3.76	18.0	33.3	29.3
16	Nil	Nil	Nil	Nil	1.44	2.25	2.21	5.47	4.39	18.1	31.1	31.7
42	Nil	Nil	Nil	Nil	1.73	2.05	2.29	6.25	4.70	17.5	24.7	31.6
96	Nil	Nil	Nil	Nil	1.80	1.08	2.62	7.18	5.17	16.9	18.9	34.9

\* Not calculable for dyes (3)–(5)

† Not calculable for dyes (4) and (5)





in the work; thanks are due to Messrs. Imperial Chemical Industries Ltd., Dyestuffs Division, for preparing the dyes used in the investigation.

SCAPA DRYERS LTD.  
BLACKBURN

(Received 28th May 1949)

### References

- <sup>1</sup> Carlene, Rowe, and Speakman, *J.S.D.C.*, **62**, 329 (1946).
- <sup>2</sup> Stevens, Private communication; Race, Unpublished investigation.
- <sup>3</sup> Robinson and Mills, *Proc. Roy. Soc.*, **A 131**, 576 (1931).
- <sup>4</sup> Drew and Fairbairn, *J.C.S.*, 823 (1939).
- <sup>5</sup> Race, Rowe, and Speakman, *J.S.D.C.*, **62**, 372 (1946).

## CORRESPONDENCE

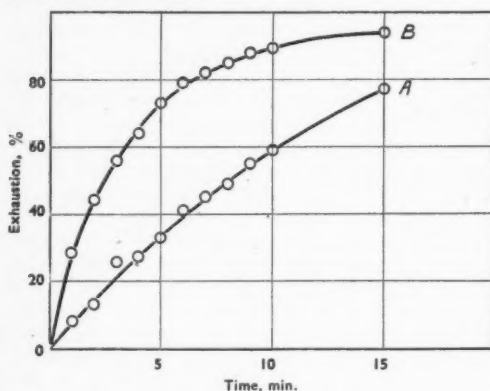
*The Editor does not hold himself responsible for opinions expressed by correspondents*

### Rate of Dyeing—Experimental Conditions

*The Editor,*

SIR,

A multitude of papers on the rate of dyeing have been published in recent years, but in spite of this amount of work the influence of the experimental conditions has not been clarified. Every investigator is now more or less compelled to procure his own figures for dyeing rates, because the variation in experimental conditions is too large to allow him to use already published data. Therefore his conclusions will necessarily rest on a too narrow basis. The purpose of this note is to give an example of how experimental conditions can affect the results.



Our graph shows the exhaustion curves for Brilliant Lanafuchsine 2G on a sample of wool in two different forms. In experiment A we used small squares ( $15 \times 15$  mm.) of a worsted fabric, and in B short lengths (1–3 mm.) of fibres from the same fabric. The difference in surface area between these two forms is negligible. The conditioned sample (0.5 g.) was weighed out and stirred in 500 ml. of the dye liquor. The total amount of dye was 2% of the weight of the material. The pH in the bath was 3 and the dyeing temperature

80°C. At definite time intervals aliquots of the dyeing liquor were taken out and measured photometrically. The time of half dyeing was 8.0 min. in A and 2.5 min. in B. This means that the diffusion of the dye in the liquid into the fabric and the yarns is much slower than the diffusion into the fibres. It is always the slowest process that determines a reaction rate, so when fabrics or yarn are used, it is the liquid diffusion that is measured. Changes of fabric construction will affect the results appreciably, while a small change in fibre condition will fall within the limits of experimental error. In order to obtain results that can be reproduced in different laboratories and used as definite values it is necessary to measure these two factors separately. The best method would be to use a standardised fibre material for the evaluation of different dyes.

The separation of all factors influencing the dyeing is of both theoretical and practical interest. In order to interpret dyeing curves in terms of fibre diffusion the diffusion in the liquid must be eliminated. On the other hand these two factors are combined in different ways, for instance in top and piece dyeing. By eliminating the form of the material one can learn much more about the dyeing properties of the fibres, the influence of the scouring, the function of the auxiliaries, etc.

The proposed method gives very good reproducibility. The rate of stirring is not critical. A similar method has recently been used for scouring trials<sup>1,2</sup>.

Our thanks are due to our company for permission to publish this report.

Yours faithfully

H. OLERUP  
J. LINDBERG

MAB OCH MYA  
MALMÖ  
SWEDEN

7th December 1949

- <sup>1</sup> Powney, J., and Fenell, A. J., *Research*, **2**, 331 (1949).
- <sup>2</sup> Bartholomé, E., and Buschmann, K. F., *Melliand Textilber.*, **30**, 249 (1949).

## Notes

### Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 14th December 1949, the proceedings included the following items of interest—

CHEMICAL SOCIETY JOINT LIBRARY COMMITTEE—Mr. J. Blair was nominated to represent the Society on this committee during 1950.

COMPOSITION OF THE COUNCIL—It was reported that four Vice-presidents would retire in March

1950, viz. Mr. H. Foster, Mr. D. B. F. McAndrew, Dr. H. A. Thomas, and Mr. G. M. Williams. Among Ordinary Members of Council only two, viz. Dr. P. W. Cunliffe and Mr. R. J. Hannay, were due to retire, and these with one unfilled casual vacancy would yield only three vacancies for the 1950 election, while five would be due to retire in 1951.

**PHOTOCHEMISTRY SYMPOSIUM**—The report of the Photochemistry Symposium Committee was adopted, and a vote of thanks accorded to the Committee for its services.

**REPORT OF SOCIETY'S MEDAL COMMITTEE**—The recommendation of the Committee that the Society's gold medal be awarded to Dr. S. M. Neale (J.S.D.C., 66, 7 (Jan. 1950)) was approved.

**MEMBERSHIP**—Twenty-eight applications for ordinary, and seventeen for junior, membership were approved.

### Meetings of Council and Committees January

Council—11th

Finance—11th

Publications—17th

*Colour Index* Editorial Panel—10th

Historical Records—4th

Terms and Definitions—6th

Summer School—12th

### George Edward Holden Commander of the Order of the British Empire

Members of the Society will be gratified by the announcement in the New Year's Honours List of the award to Mr. Holden of the C.B.E., and will wish to be associated with Council in congratulating our President on this well merited honour.

### Photographs of Presidents

Before the war it was the custom to publish a photogravure reproduction of the portrait of the President of the Society with the *Journal*. Council has decided that in future the photograph of the President will be published in the issue of the *Journal* containing the report of the Annual General Meeting at which he is elected to his first year of office. As the last portrait to be issued was that of Dr. C. J. T. Cronshaw (1939–1946) in January 1940, a photograph of Dr. C. M. Whittaker (1946–1948) appears in this issue, while one of Mr. G. E. Holden, the present President, will appear in March.

### Wool Industries Research Association Appointment of Dr. A. B. D. Cassie

The Council of the Wool Industries Research Association has selected A. B. D. Cassie, Esq., M.A., Ph.D., D.Sc., F.Inst.P., to be Director of Research. Dr. Cassie has for some years been head of the Physics Department of the Association, and during the last two years its Deputy Director of Research.

## OBITUARY NOTICE

### Victor Hoffman Majerus

Victor Majerus, who died on 21st August 1949, was born at Milnsbridge, Huddersfield, on 10th May 1885, son of John Majerus, a native of Luxemburg. His mother was a member of the Wood family, well known in Yorkshire in musical circles.

Victor Majerus was educated at Hipperholme Grammar School and Bradford Technical College. After completion of his studies, he joined the staff of The Bradford Dyers' Association Ltd., and remained with the firm all his life, except for a time during the 1914–18 war, when he was seconded to H.M. Factories, making high explosives. He was assistant to his father, who was in charge of H.M. Factory, Low Moor. Unfortunately, the works were completely destroyed by a series of explosions and fire in August 1916 with considerable loss of life. Victor Majerus, however, was at the time on holiday. His father died a few days after the explosion as a direct result of the catastrophe. The two Majerus's built up Low Moor Munitions Co. Ltd. to a high capacity, and the disaster was a great tragedy for this country at that time.

After the war, Victor Majerus continued as Manager at the Low Moor Chemical Co., and later was transferred to the B.D.A.'s head laboratories until his retirement.

He was a man of ideas and most thorough in all his work. He was never satisfied until he had satisfactorily completed an investigation, and had got the operation not only completed in the laboratory but transferred to practical operation at one of the Association's branches. He was a man of great integrity and was always endeavouring to help other members of the staff. He was a wonderfully helpful colleague, respected and loved by all members of the staff, particularly the younger laboratory assistants, whom he was always ready to advise and help, even when his investigations were necessitating his working many hours over the usual laboratory hours and even at week-ends.

During the period prior to World War I, he did a great deal of investigatory work on mercerisation and caustic soda recovery, and no man in the industry at that time knew more about this subject.

On more than one occasion did he say that work was his hobby; but for all that, he was a great sportsman. In the last war he was a member of the Special Constabulary and undertook his duties conscientiously and seriously, even when he was suffering considerably.

He married Evelyn Atkinson, daughter of William Atkinson, and after his marriage became interested in the Wyke Gospel Temperance Mission,

and later became a very active member of the church, being a very strict teetotaler.

He was interested in music, particularly amateur operatic work. He was also a great humanitarian and spent much of his leisure on welfare work for the old folk of his village.

In 1913 he became a member of the Society of Dyers and Colourists, and was a member of the Publications Committee from 1929 to 1946; he was particularly sincere in this work, dealing with the revisions with that same care and thoroughness which he displayed in all spheres of his activities.

For the last few years of his life, he was visibly failing in health, but he loved his job so much that he did not wish to retire. However, ill-health forced his retirement at the age of 63, and he died a few months later.

He suffered much during the latter years of his life; never complained, but fought on believing he would regain his former vigour. His home life was one of complete happiness—he was a devoted husband and a father revered and beloved by his family.

He leaves a widow, a daughter, and two sons.

H. H. BOWEN

## Reports on German Industry

### I.G. Farbenindustrie A.-G., Offenbach/Main Manufacture of Dyes and Intermediates and their Analysis

FDX 616\* (PB 70,423; Microfilm E 20).

Manufacturing instructions, in German, are given for the following Fast Colour Bases—Blue BB; Bordeaux GP; Kanji; Orange R; Red B, 3GL, and RL; Scarlet G and GGM; the following Fast Colour Salts—Black B; Blue B; Bordeaux GP; Orange GR; Red AL, 3GL, and RC; Scarlet R; Yellow GC and for Rapidogen G, Developer ONL and ONLK and many Palatinols and intermediates for azo dyes. Numerous analytical methods for intermediates and dyes are given. C. O. C.

### I.G. Farbenindustrie A.-G., Ludwigshafen Manufacturing Directions for Dyes, Intermediates, Resins, Plasticisers, etc.

FDX 662\* (PB 73,616; Microfilm M 106).

A microfilm of copies of works instructions, in German, for making 49 different intermediates, resins, plasticisers, etc. and for Ergansoga Brown 3RN and Fast Scarlet G Base new. C. O. C.

### Anorgana G.m.b.H., Gendorf Laboratory Reports on Experimental Research and Testing of Competitors' Dyes

FDX 645\* (PB 73,490; Microfilm B 5).

A large number of reports, written in German during 1931-34, on work done in the I.G. Gendorf laboratories, many of them dealing with the analysis and testing of Swiss, German, French, British, and American competitors' dyes. Other reports deal with—(1) X-Ray examination of dyes. (2) Analysis of food dyes. (3) Adsorption analysis of dyes. (4) Dye splitting with concentrated nitric acid. (5) Investigation of Kaya or Casha (*Memerylon medule*) leaves, used in India as a mordant for alizarin. (6) Composition and properties of Sarakatti, Khar, Kalkaram, and Olamankaram, earths used in India as auxiliaries in alizarin dyeing. (7) Experiments on banknote printing using photoactive zinc sulphides, alkaline-earth phosphors, and radioactive luminescent compounds. (8) Review of the carbon black problem in 1932. (9) Influence of alkyl groups in complex chrome dyes of the Palatine Fast Yellow 3GN type. (10) Azo dyes from hydroxyquinolines. (11) Basic dyes of the Malachite Green

series from *sec.*-arylamines substituted in the *ortho* position. (12) Chalking of Titanium White. (13) Defective fastness to light of zinc sulphide pigments due not to impurities but to the particular manufacturing process used. In addition the commercial preparation of Fluorol OV, by condensing 2 mol. of benzanthrene obtained from  $\alpha$ -benzylnaphthalene, is described. C. O. C.

### Vereinigte Glanzstoff Fabriken Viscose Rayon

FDX 667\* (PB 74,187; Microfilm D 298).

A microfilm, in German, of monthly reviews for Nov. 1939-Dec. 1944 of experimental work done in the companies' various works. There are also 15 reports written in 1945 dealing mainly with the problem of reducing the swelling properties of viscose rayon. C. O. C.

### I.G. Farbenindustrie A.-G., Ludwigshafen Tanigans and other Tanning Agents—Diffusion Measurements on Vat Dyes in presence of Peregal O

FDX 658\* (PB 73,591; Microfilm M 104).

Among 24 reports, in German, 7 deal with developments in the manufacture of the Tanigans and other tanning agents. Another by Valko describes diffusion measurements on Indanthren Brilliant Green FFB vats containing Peregal O. C. O. C.

### I.G. Farbenindustrie A.-G., Ludwigshafen Leather Dyeing and Processing and Agents therefor

FDX 672\* (PB 74,739; Microfilm M 110).

A microfilm of 40 reports, in German, mostly dealing with the tanning and finishing of leather. The following subjects are also dealt with—preparation of some Fanal colours, dyeing of Igelon NN fabrics, pigmentation of lacquers for rubber, dyes for synthetic rubber, Corial colours for leather, Corial Blue ERL. There are two general reports on the dyeing of leather and one on the dyeing of chrome-tanned glove leather. C. O. C.

### I.G. Farbenindustrie A.-G., Ludwigshafen Methods of Analysis

FDX 638\* (PB 70,066; Microfilm G 26).

A collection of 178 methods of inorganic and organic analysis used in various I.G. works. C. O. C.

\* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

## Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

### I—PLANT; MACHINERY; BUILDINGS

#### PATENTS

**Thread-advancing Devices.** Algemeene Kunstzijde Unie N.V. B.P. 627,843.

A thread-storage, thread-advancing device for carrying artificial filaments during aftertreatment comprises an outer cage consisting of a number of bars, inside which is mounted independently a frame carrying several spur gears

with axes parallel to the outer cage axis. One or more teeth of these gears project slightly beyond the cage bars. The crowns of the teeth have screw threads enabling a filament to be guided round the peripheral bars by the projecting threaded tooth, and on rotation to be advanced to the remote end. To permit if necessary thread shrinkage during aftertreatment, the bars and gears may taper slightly towards the end remote from the shaft housing.

J. W. B.



**Drying Rayon Cakes by Dielectric Heating.** Radio Corp. of America. B.P. 629,979.

**Continuous Treatment of Flocculous Textiles with Exclusion of Air.** Algemeene Kunstzijde Unie N.V. B.P. 629,100.

The apparatus comprises a conveying path consisting of several bars forming a grid and sprays for liquor. The treating chamber is closed except for two liquid seals. The conveyor bars are bent in V shape immediately before reaching the liquid seals so that they can pass through them. C. O. C.

**Drying a Tow of Artificial Fibres.** Courtaulds Ltd. and R. L. Wormell. B.P. 629,818.

The tow is passed on an endless conveyor through a drying chamber and is then withdrawn from the conveyor vertically downwards from the underside of the tow, which reduces the tendency of the tow to become entangled during withdrawal. C. O. C.

**Drying Loose Fibres.** G. Paggi. B.P. 627,222.

The fibres are carried through the machine by hot air which flows successively through several ducts. The ducts have means for periodically reversing the direction of flow of the air, flap-type gratings, lattice screens or adjustable baffles, and/or one or more local enlargements in cross-sectional area so as to arrest or vary the flow of the fibres. The rate of flow of the fibres is thus rendered independent of that of the hot air, so that by varying the speed of the air in a particular duct region it conveys only the drier fibres, viz. those of lower sp. gr., and not the wet ones. C. O. C.

**Waxing Yarns.** M. B. Coleman, J. R. Bennington, and American Viscose Corp. U.S.P. 2,474,346.

Apparatus for applying wax or other solid lubricants to yarn. C. O. C.

**Cheese Dyeing.** M. E. Bachleda. U.S.P. 2,474,967.

Yarn is wound on to a core formed by a helical coil spring covered with a sleeve fabric or may be transferred from a bobbin, etc., on to such a core. When the dye liquor passes through the package the spring is compressed or contracted longitudinally to its axis, so that the liquor can more thoroughly penetrate the wound yarn. The fabric sleeve must have an internal diameter at least as small as the external diameter of the spring. The diameter of the spring is contracted while the yarn is being wound on it or during transfer of wound yarn on to it or withdrawal of the spring, by increasing the number of convolutions of the spring. By this means, although the spring becomes embedded in the fabric sleeve or yarn during the dyeing, it is readily removed. C. O. C.

**Registering Webs being longitudinally fed to Machines.** Kustner Frères & Cie. S.A. B.P. 628,154.

**Treating Fabrics with Liquids.** Sellers & Co. (Huddersfield) Ltd. and E. R. Sellers. B.P. 629,310.

The nip rollers are hydraulically weighted so that the upper roller can exert any desired pressure upon the lower roller. The machine is suitable for treating endless fabrics. C. O. C.

**Continuous Open-width Wet Treatment.** Ver. Färbereien & Appretur A.-G. B.P. 630,160.

The fabric is guided, during its introduction into the liquor, between two regulated jet combs directed towards one another. The strength of the jets is such that they only guide the fabric and exert no conveying action on it. The fabric is drawn through the liquor with a sliding movement over convex guides. On leaving the bath it is subjected to a further sliding and spraying action. C. O. C.

**Treating Endless Felts, etc.** Orr Felt & Blanket Co. B.P. 627,857.

Endless felt or the like is processed by supporting one portion of it in a treatment chamber and another portion outside the chamber; successive portions of the felt being repeatedly passed through the chamber, where they are heated while cooling that portion which has just emerged from the chamber. The felt is stretched longitudinally during heating and cooling. C. O. C.

**Washer for Cloth-covered Rollers.** R. H. Mort. B.P. 627,876.

A simple and efficient washer is described which thoroughly cleanses cloth-covered rollers without any tendency to get them "out of round". C. O. C.

**Fabric-drying Machine.** B. R. Andrews. U.S.P. 2,473,629.

Quick drying is obtained by projecting high-temperature radiant heat on the cloth at the same time that hot air is blown on it. C. O. C.

**Heating the Drying Cylinders of a Papermaking Machine.** Papierfabrik Balsthal A.-G. B.P. 627,811.

If hot water is used instead of steam it enables easier and more accurate control of the temperature gradient along the drying range. It enters the drying range about two-thirds of the way along and is divided into three flows, two passing in the direction opposite to that in which the web is going through the upper and lower cylinders respectively, and the third passing in the direction of travel of the web through the other cylinders in succession. C. O. C.

**Driving Mechanism for Calender Rollers.** John Galloway & Co. Ltd. and J. Butler. B.P. 627,939.

The power drive for calender rollers has means whereby the driving spindle for the bottom roller can be manually operated when the power drive is disengaged. C. O. C.

**Calender.** J. Haydock. B.P. 629,079.

Each calendering roll has a bed of flexible metal plate bent to conform with the bottom portion of the roll. Sheet metal is welded to the bottom side of the bed so as to provide separate steam channels extending across it. Such a bed closely "hugs" the roll. C. O. C.

**Silk-screen Printing Machinery.** R. W. Hinks. B.P. 628,362.

The screen pivots on a supporting frame, there being mechanical means to tip the screen. The driving device for the squeegee is synchronised with the tipping of the screen, there being an automatic lift at the end of the stroke to enable the squeegee to pass over the puddle of printing paste and come behind it for the return stroke. C. O. C.

**Printing Selvedges in Two or More Colours.** A. Reggiani. B.P. 627,868.

Manually operated apparatus for dry stamping on selvedges or garments by means of inked ribbons has mounted, on a vertically reciprocable slide of the stamp, a frame, and several shafts supported on the frame for receiving rolls of inked ribbons of different colours. The ribbons are guided side by side between the stamp and a counter-stamp in a direction transverse to that in which the selvedge or garment is displaceable over the counter-stamp. The ribbons are advanced simultaneously during the inoperative movement of the stamp, which is operated by a lever or pedal to make simultaneously separate impressions by each of the ribbons. The ribbon-advancing means is automatically actuable during the inoperative movement of the stamp. C. O. C.

**Nylon-preboarding Machine.** L. Heldmaier and British Schuster Co. Ltd. B.P. 628,286.

Nylon stockings are continuously preboarded or plasticised by mounting on forms carried by an endless conveyor through a plasticising chamber, in which treatment with hot air and moisture takes place. The desired moisture is mixed with hot air, and the mixture introduced evenly along the length of the chamber via spaced ducts at the bottom of the chamber, and afterwards led away at the top. Moisture may alternatively be introduced by spraying the hose prior to or after entering the chamber or by heating the liquid in a trough within the chamber. G. E. K.

**Drum-type Washing Machine.** Prosperity Co. Inc. B.P. 629,026.

A simple and efficient construction is described in which an inner goods receptacle is actuated by rollers on which it rests as the rollers run in the washing liquor. It has all the advantages of a shell-less washer and none of the disadvantages. C. O. C.

**Drum-type Washing Machines.** Co-operative Wholesale Society Ltd. and J. R. Moore. B.P. 629,259.

**Unloader for Drum Washing Machines.** Prosperity Co. Inc. B.P. 629,027.

**Steam-spotting Boards.** Isaac Braithwaite & Son Engineers Ltd. and R. E. English. B.P. 629,826.

The board is pivoted about midway along its length on a stand; One end of the board is connected to the valve

supplying steam to the spotting gun, so that the valve is operated by slightly pressing the opposite end of the board. C. O. C.

**Laundry Ironing Machine.** Horton Manufacturing Co. B.P. 629,197.

**Rotary Ironers.** British Thomson-Houston Co. Ltd. B.P. 629,888.

**Ink-drying Burner for Printing, Paper-coating, etc. Machines.** C. M. Kemp Manufacturing Co. B.P. 629,269.

**Adding Powdered Dyes to Liquids.** C. C. Keane and Great Lakes Pipe Line Co. U.S.P. 2,473,474.

Apparatus for adding powdered dye to liquids, particularly hydrocarbons in bulk, consists of a funnel which can be inverted over the open top of the drum containing the dye and secured to it. This assembly is then placed in an inverted position in a stand, and the mouth of the funnel connected to the vessel containing the liquid to be coloured or to the pipe through which it is flowing. A sleeve of dust-proof fabric is attached to the rim of the funnel and extends over the sides of the dye drum, against which it is firmly held by an elastic garter. C. O. C.

## II—WATER AND EFFLUENTS

### PATENTS

**Removing Suspended or Colloidal Impurities from Water.** Permutit Co. Ltd. and J. G. Milton. B.P. 627,892.

Apparatus for dealing with water, the rate of flow of which may vary considerably, is described. C. O. C.

**Purification of Liquids by Sedimentation.** W. Paterson. B.P. 630,505.

An upflow liquid treatment tank is divided into low turbulent and upper quiescent chambers by a diaphragm having in it numerous flow-restricting orifices of upwardly expanding trough or funnel shape. The total minimal cross-sectional area of the orifices is less than the horizontal cross-sectional area of the liquid in the lower chamber. This ensures uniform upflow from the turbulent to the quiescent chamber at the inflow rate. C. O. C.

**Clarifying Water.** Lever Brothers & Unilever Ltd. and H. J. Wheaton. B.P. 628,081.

Suspended solid matter in water is coagulated by adding a solution of activated sodium silicate (i.e. a very dilute solution which has been incompletely neutralised by an acid so as to produce negatively charged colloidal hydrated silica) and electrolytically producing a flocculent gelatinous hydroxide of aluminium, iron, or magnesium in the water. Thus the activated sodium silicate is run continuously into a stream of the raw water immediately before it passes between an anode of aluminium, iron, or magnesium and a suitable cathode. The process is applicable over a wide pH range, there is no increase in the soluble-salt content, there are no mechanical difficulties in accurately proportioning the reagents, and no acid-proof plant is required for preparing the reagents. C. O. C.

**Treatment of Scouring Effluents.** Fields Point Manufacturing Corp. B.P. 627,873.

Raw-wool scouring effluents are treated with sufficient bleaching powder to deposit calcium curds and destroy protein material. The curd-containing liquor is centrifuged to separate the light and heavy curds, which after further hydroextraction are acid-treated to obtain fatty by-products. J. W. B.

## III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

**Acidimetric Properties of Soaps.** J. P. Wolff. *Olagineux*, 4, 141-144 (1949): *Chem. Abs.*, 43, 6886 (25th Sept. 1949).

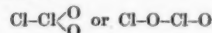
Tenfold dilution of the buffer system oleic acid-sodium oleate-water (0.1N.), contrary to expectation, increases the pH; this and the titration curves of soap solutions suggest the existence of dimeric ions or molecules. More dilute solutions conform to theory and are used for determining the solubility of the acid. Data for oleic, palmitic, lauric, and abietic acids are given. C. O. C.

**Constitution, Application, and Evaluation of Textile Chemicals.** G. Schwen. *Melliand Textilber.*, 30, 351-359 (Aug. 1949).

Both inorganic and organic chemicals used in the textile industry are classified according to their chemical constitution, field of application, and methods of evaluation. Auxiliary products for use in the processing, dyeing, and finishing of textiles are discussed in detail. B. K.

**Applications of Radioactive Chlorine to Study of Mechanisms of Reactions Involving Changes in the Oxidation State of Chlorine.** H. Taube and H. Dodgen. *J. Amer. Chem. Soc.*, 71, 3330-3336 (Oct. 1949).

Using radioactive chlorine as a tracer, it was observed that—(a) Oxidation of chlorite by chlorate in acid is much slower than the disproportionation of chlorite. (b) When chlorite reacts with chlorine (or hypochlorous acid) to form chlorine dioxide or chlorate and chloride ion, most of the chlorine atoms in the chlorine dioxide or chlorate are derived from the chlorite. (c) In the production of chlorine and chlorine dioxide from chloride ion and chlorate ion in acid, the chlorine atoms in the dioxide are mostly derived from the chlorate. (d) In the disproportionation of chlorite in acid catalysed by chloride ion, the chlorine atoms in the chlorine dioxide are mostly derived from the chlorite. (e) In each of (b), (c), and (d) a small but definite degree of mixing of the chlorine atoms in the products has occurred. (f) The reverse reaction in system (c) near its equilibrium composition is very slow. (g) Exchange of chlorine activity between  $\text{ClO}^-$  and  $\text{ClO}_2^-$  in base is very slow. (h) Exchange of chlorine with chlorate ion in acid at room and elevated temp. is very slow. An unsymmetrical intermediate—



common to systems (b), (c), and (d) is postulated.

C. O. C.

### PATENTS

**Dispersing Agents.** H. Schou. B.P. 494,639.

This is an amended specification. The products obtained by esterifying a polymerised higher fatty acid with a polyglycerol are dispersing agents which may be used for producing either water-in-oil or oil-in-water dispersions or emulsions. C. O. C.

**Emulsifying Compositions.** R. G. Mitchell, H. C. Tait, C. L. Gilbert, W. David, Eagle Oil & Shipping Co. Ltd., and Shell Refining & Marketing Co. Ltd. B.P. 628,766.

Residues soluble in alcoholic alkali, from the sulphuric acid petroleum refining process are extracted with petroleum ether to dissolve out a component which, when mixed with water-soluble long-chain sodium alkyl sulphates, e.g. Teepol X, forms useful emulsifying agents for oils. J. W. B.

**Emulsifying Compositions.** Shell Refining & Marketing Co. Ltd., P. J. Garner, and P. A. Winsor. B.P. 629,139.

Stable oil-water emulsions are formed by using an emulsifying composition comprising a synthetic organic emulsifying agent, having a greater solubility in or affinity for water than oil, and an alkane-1:2-diol containing > 6 C. J. W. B.

**Wetting, Dispersing, Washing, or Softening Agents or Dyeing or Textile Assistants.** Ciba Ltd. B.P. 630,492.

An aliphatic carboxamide or an aliphatic methane (1 mol.), containing at least one H bound to amide N, is heated with an inorganic bisulphite (not < 1 mol.) and an aldehyde containing at least one sulpho group in the form of a water-soluble salt (1 mol.) or with an inorganic bisulphite (not < 2 mol.) and an aldehyde containing an ethylenic bond (1 mol.), if desired in presence of an inert solvent or, as catalyst, a little of a secondary amine. The products are useful as low-mol.-wt. wetting agents soluble in mercerising lye. Those products containing an aliphatic residue of > 7C are particularly useful as wetting, dispersing, washing, or softening agents or as dyeing assistants. They also prevent the agglomeration of cellulose fibres when making staple fibre from regenerated cellulose. They have good resistance to hard water, in which they have better detergent action than

compounds of similar nature which contain only one sulpho group. C. O. C.

**Germicidal Detergent.** F. C. Bersworth.

U.S.P. 2,474,412.

A mixture of 10–30% of an alkali-metal salt of ethylenediaminetetraacetic acid and not > 25% of a quaternary ammonium salt of that acid (the quaternary ammonium cation being germicidal), made up to 100% with alkali-metal phosphates and/or carbonates and/or silicates and/or borates and/or sulphates, is used. C. O. C.

**Starch Paste.** J. P. Casey and A. E. Staley Manufacturing Co.

U.S.P. 2,472,790.

An enzyme-thinned starch paste is obtained by making up an aqueous slurry of a starch-liquefying enzyme and several starches so modified that their enzyme-converting temperatures are lowered by about 15°r. The starches are selected so that there is a difference of not < 15°r. between the enzyme-converting temperatures of any pair of them. The slurry is then heated to thin each starch in turn, starting with the one having the lowest enzyme-converting temperature. This avoids the starch paste passing through a troublesome thick stage before thinning out to the desired fluidity. C. O. C.

**Preventing Hydrophilic Colloids from Swelling during Washing.** W. D. Ramage and U.S. Secretary of Agriculture.

U.S.P. 2,474,367.

Hydrophilic colloids whose swelling power increases as the amount of electrolyte present decreases, e.g. gum tragacanth, alginates, etc., are washed from electrolytes by treating with an aqueous solution of an ammonium salt of a weak acid which vaporises below the temperature at which the colloid is degraded, e.g. ammonium carbonate, drying, and then vaporising off the ammonium salt. C. O. C.

**Polyvinyl Alcohol.** Shawinigan Resins Corp. and E. Lavin.

B.P. 629,695.

Polyvinyl acetate-alcohol is prepared in a form which gives aqueous solutions of high viscosity by hydrolysing polyvinyl acetate with sulphuric acid dissolved in a mixture of methanol (3–25%) and either benzene, toluene, or xylene (97–75%) until the product contains 15–40% polyvinyl acetate. Discoloration of the product on heating is prevented by treating with a solution of an alkaline material, e.g. potassium acetate, in methanol. The products are suitable as thickening agents, protective colloids, etc. E. C.

**Aqueous Binding Agents.** Ciba Ltd.

B.P. 627,301.

Acid casein is dissolved with the aid of an alkaline substance, urea and/or thiourea, and formaldehyde. The solution is then heated until a colloidal mixed condensate is formed, which as soon as it becomes thick and before it becomes insoluble is diluted with water and immediately cooled. The product is stable and is used as a binding agent, e.g. in textile printing pastes, which becomes water-resistant on being heated. C. O. C.

**Binding Agents for fixing Pigments on Fibrous Materials.** Ciba Ltd.

B.P. 628,882.

The products obtained by the process of B.P. 544,157 (cf. J.S.D.C., 58, 174 (1942)) have the disadvantage that they contain large quantities of formaldehyde; this can be avoided by using water-soluble ethers of hydroxymethyl compounds of amides instead of the hydroxymethyl compounds themselves. C. O. C.

**Water-dispersible Quaternary Ammonium Compounds—Wetting, Softening, Emulsifying, and Dye-fixing Agents.** J. B. Rust and Montclair Research Corp.

U.S.P. 2,474,202.

The products obtained by interaction of a long-chain monocarboxylic acid with a polyamine and an alcohol in presence of a dehydrating catalyst and then with an alkyl halide or sulphate are wetting, softening, and emulsifying agents, some of which also render some dyeings more fast to washing, rubbing, etc. C. O. C.

**Water-repellent Composition.** Société des Usines Chimiques Rhône-Poulenc.

B.P. 628,585.

A water-repellent paste applicable to textiles, paper, ceramics, etc. consists of an organosilicon oil containing an impalpable powder, e.g. silica gel which has been water-proofed by treatment with an organosilicon derivative. C. O. C.

**Coating Materials for Waterproofing Fabrics.** H. A. Dephillips.

B.P. 627,045.

A coating material which renders fabrics resistant to high water pressure but allows them to transmit water vapour consists of a vinyl chloride copolymer of average mol. wt. 16,000–24,000; dibutoxyethyl phthalate, dibutylmono-ether of ethylene glycol phthalate, and butoxyglycol phthalate; and a pigment ground with triethylene glycol dicaprylate and some triethylene glycol diesters of other fatty acids, the mixed esters boiling at over 178–215°C./2 mm., vapour pressure not > 1 mm. at 28°C. and a water solubility of 0.089 g. in 100 g. at 25°C. C. O. C.

**Flame-retarding Coatings.** H. R. Frisch.

B.P. 629,654.

Aqueous solutions which deposit water-insoluble, flame-retarding, glossy coatings are obtained by dissolving zinc orthophosphate and/or zinc orthoarsenate in 0.3–1.5 times their weight of 35% aqueous ammonia. Small amounts of zinc, cupric, cadmium, nickelous, and/or cobaltous hydroxide may also be added. E. C.

**Mildewproofing Agent.** Nederlandsche Centrale

Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek.

B.P. 628,564.

Salicylanilide is melted with an oil-soluble emulsifying agent which lowers its m.p. and then while molten dispersed in water in presence of a stabiliser consisting of a water-insoluble hydrophilic interface-active agent or a water-soluble high-molecular interface-active agent. The resulting suspension is preferably adjusted to pH 6–8. C. O. C.

**Rotproofing Composition.** P. G. Benignus and Monsanto Chemical Co.

U.S.P. 2,476,235.

A water-in-oil emulsion containing in the oil phase a water-insoluble fungicide, e.g. Cu 8-hydroxyquinoline, a modified alkyl resin of high fatty acid: phthalic anhydride ratio, and a mixture of chlorinated diphenyls is used to render textiles, etc. permanently resistant to bacteria and fungi. C. O. C.

**Organic Mercury Compounds—Fungicides.** F. J. Sowa.

B.P. 628,525.

Fungicides for textiles are obtained by treating a compound of general formula R-Hg-O-X (R = a cyclic group, X = H or -CO-Alk), e.g. phenylmercury acetate, in aqueous medium with a compound of general formula Y-S-C< (Y = an alkali metal or ammonium residue, and the free valencies of the C are attached to two or more atoms or radicals), e.g. potassium ethyl xanthate or ammonium thiophenoxides. C. O. C.

**Organofluorosiloxanes.** Dow Chemical Co.

B.P. 627,800.

Organofluorosiloxane condensates, containing silicon atoms attached to hydrocarbon radicals and fluorine, are made by hydrolysing a compound of general formula R-SiFX<sub>2</sub> (R = a hydrocarbon radical and X = a readily hydrolysable group, e.g. Cl). They are useful for coating textiles, paper, etc. W. G. C.

**Cellulose Nitrate-Linseed Oil Composition for Impregnating and Finishing Textiles.** Svenska

Oljeslageri A.-B.

B.P. 629,268.

Cellulose nitrate is readily soluble in linseed oil which has been refined with 2–3% of its weight of 35–80% aqueous sulphuric acid and then blown with air at < 150°C. C. O. C.

**Laminating Resin.** R. G. Roberts, R. Hammond, and I.C.I. Ltd.

B.P. 629,015.

A mono- or dihydroxyalkyl ester of an acrylic acid, e.g. glycerol monomethacrylate, is condensed with a compound containing two radicals selected from—hydroxymethyl, alkoxymethyl, isocyanate, or isothiocyanate, e.g. dimethylolurea. The products are suitable as laminating resins and are rapidly cured by heating in presence of a polymerisation catalyst, e.g. benzoyl peroxide. E. C.

**Laminating Resin.** R. Hammond and I.C.I. Ltd.

B.P. 629,019.

A mono- or polyhydroxyalkyl ester of an acrylic acid, e.g. β-hydroxyethyl methacrylate, is treated with phosphene, and the acryloyloxyalkyl chloroformate obtained is treated with a polyhydroxy alcohol, e.g. glycerol or pentaerythritol. The viscous products are suitable as laminating resins, and are rapidly cured by heating in presence of a polymerisation catalyst, e.g. benzoyl peroxide. E. C.



**Dry-cleaning Solvents.** H. W. Kay. *B.P.* 630,278.

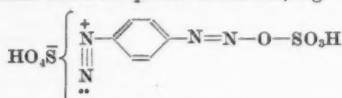
Water is incorporated into a dry-cleaning agent by mixing with the dry-cleaning solvent an emulsion of paraffin hydrocarbon and water containing a saturated or unsaturated fatty acid, e.g. stearic or oleic, or a glyceride thereof, and an alkylolamine. The products will remove water-soluble stains which are difficult to remove by usual dry-cleaning methods. J. W. B.

**IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS****Quantum-mechanical Treatment of Dyes with Branched Electron Gas.** H. Kuhn. *Helv. Chim. Acta*, 32, 2247-2272 (Dec. 1949).

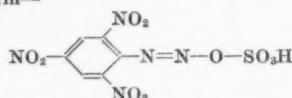
The positions and intensities of the absorption bands of a series of dyes have been evaluated on the fundamental simple assumption that the loosely bound  $\pi$ -electrons behave as a one-dimensional electronic gas extended over a large part of the dye molecule. The potential energy along the branched orbit is regarded as constant. Good agreement with the experimental data has been found for dipyrindyl violet, disodium stilbene, and Wurster Blue. H. H. H.

**Influence of Water on the Coupling Power of Diazotised Amines and on Diazo-group Elimination in Aqueous Ethanol-Sulphuric Acid Media.** H. H. Hodgson and J. Ratcliffe. *J.C.S., Supplementary Issue No. 1*, S233-S234 (1949).

The diazo compounds of the 2:6-dihalogeno-4-nitroanilines have been coupled in aqueous sulphuric acid of various concentrations with  $\beta$ -naphthol in ethanol, and also decomposed by copper powder and by cuprous oxide, which appear to be equally efficient, in the same set of aqueous ethanolic media. The amount of coupled product decreased by approx. 10%, whereas the efficiency of diazo-group replacement increased by approx. 40% as the water content progressively increased. This result is in accord with Schoutissen's conclusions (*J. Amer. Chem. Soc.*, 55, 454 (1933)) that strongly electrophilic groups promote covalent diazo-compound formation, e.g.—



in strongly acid solution, and further support is afforded by the fact that diazotised picramide could be coupled but not deaminated under the same conditions by either copper or cuprous oxide, and so must be predominantly in the covalent form—



2:4-Dinitro-1-naphthylamine and 1:6-dinitro-2-naphthylamine have been found to deaminate efficiently under conditions hitherto regarded as promoting diazo-oxide formation (cf. Hodgson and Birtwell, *J.C.S.*, 433 (1943)). The yields of dihalogenonitrobenzenes from 2:6-dihalogeno-4-nitroanilines are higher than those hitherto recorded. H. H. H.

**Dipole Moment and Spectrographic Data for Certain Diazophenols and Diazonaphthols.** J. D. C. Anderson, R. J. W. Le Fèvre, and I. R. Wilson. *J.C.S.*, 2082-2088 (Aug. 1949).

The dipole moments and ultra-violet spectra of 3:5-dibromo-1:2-benzoquinone-2-diazide, 1:2-naphthaquinone-1-diazide, 1:2-naphthaquinone-2-diazide, 4-nitro-1:2-naphthaquinone-1-diazide, 1:4-naphthaquinone-diazide and *p*-benzoquinonediazide indicate that quinonoid structures contribute predominantly to the real structures, in contrast with benzthiadiazole, for which a cyclic formulation seems satisfactory. Data for "azibenzil" are also included. H. H. H.

**Formation of Isomeric Azo-compounds in the Coupling of Diazonium Salts with 1-Naphthylamine.** H. S. Turner. *J.C.S.*, 2282-2289 (Sept. 1949).

The mixtures of the isomeric 2- and 4-arylazo-1-naphthylamines obtained by coupling diazotised aniline

and several substituted anilines (*p*-methyl-, *p*-methoxy-, *m*- and *p*-chloro-) with 1-naphthylamine have been separated by adsorption chromatography on alumina. The absorption spectra of these compounds over the range 220-580 m $\mu$  have also been determined. The chromatograms obtained were generally complex, often containing more than 12 distinct zones, the *o*- and *p*-aminoazo compounds being the principal components. There was no indication that diazoamino compounds were present in the crude coupling products, even where coupling was carried out in aqueous acetic acid-sodium acetate. When a *para*-substituted benzenediazonium salt coupled in the last named medium, the proportion of *ortho* coupling increased with the electron-releasing character of the substituent. H. H. H.

**Cleavage by Diazonium Compounds. V—*o*-Cresolphthalein.** E. Ziegler and G. Zigeuner. *Sitzungsber. Oster. Akad. Wiss.*, 158, (2), 313-314 (1949).

Phenolphthalein is split by diazonium salts into azophenols and *o*-(*p*-hydroxybenzoyl)benzoic acid, and the behaviour of *o*-cresolphthalein towards *p*-toluenediazonium chloride is found to be analogous, viz. cleavage into 2:4-bis-*p*'-toluenazo-*o*-cresol and 4'-hydroxy-5'-methylbenzophenone-2-carboxylic acid. Previous work by G. Leandri (*Gazzetta*, 78, 20 (1948)), who claimed the formation of mono- and bis-benzenazo-*o*-cresolphthalein by the reaction of *o*-cresolphthalein in alkaline solution with *p*-toluenediazonium chloride, is thus found to be in error. H. H. H.

**Unusual Light Absorption of Several Simple Indophenol Dyes.** H. Schulze. *Z. Naturforsch.*, 2b, 400-404 (1947); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

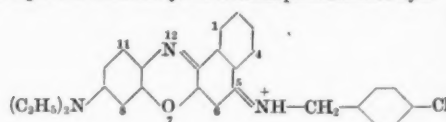
In coupling *NN*-diethyl-*p*-phenylenediamine with a 1:2-hydroxybenzanilide having a strongly polar group on the *N*-ring, a purple dye can be obtained instead of the usual blue-green. Thus, 6-hydroxy-4:5-dimethylbenzanilide when coupled yields a blue-green dye, whereas 2-(6'-hydroxy-4':5'-dimethylbenzamido)-benzoic acid yields a dye with an absorption maximum at 545 m $\mu$ . Eighteen examples are given. C. O. C.

**Preparation of Indulines.** R. Stahl. *Teintex*, 13, 445 (Dec. 1948).

Modification of O. Witt's process for the production of Induline by the action of aniline on Orange IV has shown that other varieties of Induline are obtained when the aniline is replaced by *a*-naphthylamine, glycerol, or acetin. B. K.

**Halogenated Benzophenoxazine Dyes.** H. A. Sloviter. *J. Amer. Chem. Soc.*, 71, 3360-3362 (Oct. 1949).

The 5-*p*-halogenobenzylamino-9-diethylamino-benzo[a]phenoxazine chlorides and corresponding 5-allylamino compound have been prepared as well as the intermediate *N*-*p*-halogenobenzyl-*a*-naphthylamines and *N*-allyl-*a*-naphthylamine. *N*-*p*-Iodobenzyl-*a*-naphthylamine cannot be prepared by treating *N*-*p*-aminobenzyl-*a*-naphthylamine with nitrous acid and iodide. Treatment of 5-bromo-1-naphthylamine with 2-nitroso-5-diethylaminophenol does not yield a benzophenoxazine dye.



C. O. C.

**Replacement of Substituents in Derivatives of meso-Benzanthrone.** W. Bradley. *J.C.S.*, 2712-2715 (Oct. 1949).

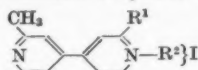
The intermediate formation of the 4-mesobenzanthronyl anion during the conversion of mesobenzanthrone into 4:4'-dimesobenzanthronyl implies that the electron-attracting effect of the carbonyl group is very readily transmitted through the component naphthalene nucleus. This accords with the development of an intense orange-red colour when mesobenzanthrone is dissolved in concentrated sulphuric acid, with the occurrence of deeply coloured alkali derivatives of 3-, 4-, and 6-acylamino-mesobenzanthrones, with the mobility of halogen substituents attached to position 6 of mesobenzanthrone, and with the ready hydrolysis of 6-aminomesobenzanthrone. A further example of the effect is found in the replacement, by other



amines, of amino, alkylamino, dialkylamino, aralkylamino, and arylamino groups attached to position 6 of meso-benzanthrone. The mechanism of the replacement reaction is discussed. H. H. H.

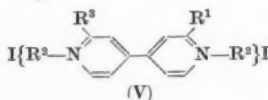
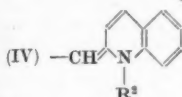
**Cyanine Dyes from 2:2'-Dimethyl-4:4'-dipyridyl.** A. B. Lal and V. Petrow. *J.C.S., Supplementary Issue No. 1*, S115-S120 (1949).

2:2'-Dimethyl-4:4'-dipyridyl alkiodides (Ia and Ib) have been converted into the *p*-dimethylaminoanils (IIa and IIb), the *p*-dimethylaminostyryl derivatives (IIIa and IIIb), and the methinecyanine (IVa); also into symmetrical and unsymmetrical trimethinecyanines. Dyes (V) have also been obtained from the diquaternary salts of the base. The mechanism of formation of cyanine dyes is discussed.



$R^1 = (a) -CH_3; (b) -C_2H_5$

$R^1 = (I) -CH_3$



$R^1 = -CH=CH-CH_2-N(CH_3)_2; R^2 = R^3 = -CH_3$

and  $R^1 = R^3 = -CH=CH-CH=CH-N-C_2H_5;$

$R^2 = -C_2H_5$



H. H. H.

**Instability of Quaternary merocyanines.** A. Van Dornael. *Bull. Soc. chim. Belg.*, 58, 403-411 (July-Sept. 1949).

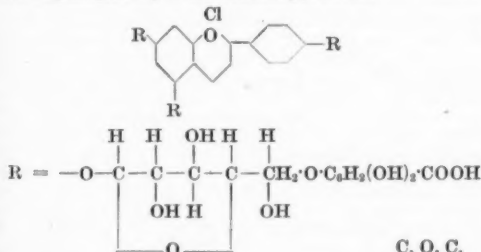
During the crystallisation of merocyanines and merocyanines from alcohol, it was found that the rhodanine nucleus was split to give a fragment of an  $\alpha$ -mercaptoamide, and that such opening of the ring was facilitated by the presence of an organic base such as pyridine or triethylamine. H. H. H.

**Yellow Direct Cotton Dye from *Polycladus abietinus* Philippi.** G. B. Marrini-Bettolo. *Ricerca sci.*, 18, 627, 628 (1948); *Chem. Abs.*, 43, 8101 (25th Sept. 1949).

Extraction of this high Andean plant with organic solvents gives a 20-30% yield of an intensely yellow substance, the methyl alcohol extract of which yields *polycladin*. This gives some of the reactions of the flavonic compounds and dyes cotton an intense yellow. C. O. C.

**Pigment of Macpalcxochitl.** E. S. Pallares and H. M. Garza. *Arch. Biochem.*, 21, 377-382 (1949); *Chem. Abs.*, 43, 7935 (1949).

The pigment of "flor de manita" or macpalcxochitl is 4':5:7-trigalloglucoxy-1-chlorobenzopyroxone—



C. O. C.

**Corticrocin, a Pigment from the Mycelium of a *Mycorrhiza* Fungus.** H. Erdtman. *Acta Chem. Scand.*, 2, 209-219 (1948); *Chem. Abs.*, 43, 6982 (25th Sept. 1949).

The yellow mycorrhiza frequently found in Sweden on the roots of pine, spruce, and *Vaccinium vitis-idaea* (fungus probably *Corticium croceum* Bres.) contains about 4% of an orange-yellow pigment, corticrocin, identified as 1:3:5:7:9:11-dodecahexaene-1:12-dicarboxylic acid. It is the first unbranched polyenedicarboxylic acid to be found in nature. C. O. C.

**Review of Inorganic Pigment Progress.** W. M. Morgans. *Paint*, 19, 377-381 (Nov. 1949).

A general review of recent literature, there being 64 references. C. O. C.

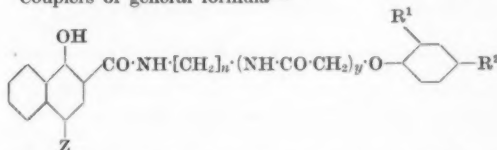
**Photosensitisation of the Internal Photoeffect in Zinc Oxide and other Semi-conductors by Adsorbed Dyes.** E. K. Putseyko and A. N. Terenin. *Zhur. Fiz. Khim.*, 23, 676-688 (1949); *Chem. Abs.*, 43, 7349 (10th Oct. 1949).

When a dye having an absorption maximum at  $\lambda$  is adsorbed on a semi-conductor, the latter shows a photoelectric effect on irradiation with  $\lambda$ , although the non-contaminated semi-conductor is sensitive only to wavelengths  $< \lambda$ . C. O. C.

#### PATENTS

**1-Naphthol-2-carboxyamide Couplers for Colour Photography.** A. Weissberger, I. F. Salminen, P. W. Vittum, and Eastman Kodak Co. *U.S.P.* 2,474,293.

Couplers of general formula—



( $R^1$  and  $R^2$  = same or different alkyl radicals of 1-5 C,  $Z = H$  or  $Cl$ ,  $n = 2-4$ ,  $y = 0$  or  $1$ ) produce blue-green images of high purity and stability on photographic development. C. O. C.

**Colour Couplers.** Du Pont. *B.P.* 629,482.

Pyrazolyl compounds, obtained by reaction of a 5-acyloxy-pyrazole-1(or 3)-carboxyl halide (the manufacture of which is described) with *m*-aminobenzaldehyde dimethylacetal or *m*-aminobenzaldehyde ethylene glycol acetal, yield dye images when used with an aromatic primary amino developing agent to develop a photographic element containing reducible silver salts. C. O. C.

***p*-Hydroxybenzyl Alcohol Couplers for Colour Photography.** P. W. Vittum, A. Weissberger, and Eastman Kodak Co. *U.S.P.* 2,476,008.

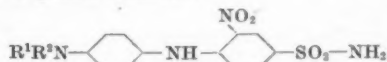
Compounds of general formula  $HO-R^1-C(OH)R^2R^3$  ( $R^1$  = *para*-linked arylene;  $R^2$  and  $R^3$  = H, hydrocarbon, or heterocyclic group) are used in presence of a primary amino developer. C. O. C.

**$\beta$ -Naphthoselenazole Compounds — Intermediates for Cyanine and merocyanine Dyes.** H. W. J. Cressman and Eastman Kodak Co. *U.S.P.* 2,475,949.

A 1-alkyl-1- $\alpha$ -naphthyl-2-selenourea is oxidised with a halogen in anhydrous carboxylic acid medium to yield a  $\beta$ -naphthoselenazole compound which can be used to prepare 2-alkylthio- $\beta$ -naphthoselenazole quaternary salts; these are very useful intermediates for cyanine and merocyanine dyes. C. O. C.

**Diphenylaminesulphonamide Dyes for Acetate Rayon.** G. W. Seymour, V. S. Salvin, W. D. Jones, and Celanese Corp. of America. *U.S.P.* 2,474,333.

Dyes of general formula—



( $R^1$  and  $R^2$  = H, alkyl, hydroxyalkyl, or acyl) dye cellulose acetate golden yellow to golden brown of superior resistance to wet or dry bleeding, light, washing, etc. Thus 4'-acetamido-2-nitrodiphenylamine-4-sulphonamide

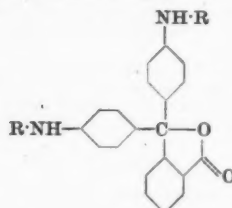
gives a golden yellow fast to light, dry bleeding, washing, and acid fading. C. O. C.

**4-Amino-1:8-naphthalimides—Acetate Rayon Dyes.** H. Z. Lecher, M. Scalera, A. W. Joyce, W. S. Forster, and American Cyanamid Co. U.S.P. 2,474,185.

4-Amino-1:8-naphthalimides dye acetate rayon and many resins yellow and give strong yellow and yellow-green fluorescence under ultra-violet radiation. Good yields of high-grade products are obtained with negligible by-products if 4-amino-1:8-naphthalic anhydride is treated with a considerable excess of a primary amine. C. O. C.

**Secondary Amines of 3:3-Bis-*p*-aminophenylphthalide.** C. S. Adams and National Cash Register Co. U.S.P. 2,474,084.

Compounds of general formula—



(R = a univalent organic radical), e.g. 3:3-bis-*p*-methylaminophenylphthalide, are normally colourless and stable but become blue in presence of a polar substance. C. O. C.

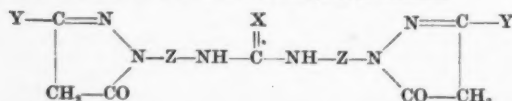
**Coloured Colour Couplers for Colour Photography.** Kodak Ltd., D. B. Glass, P. W. Vittum, and A. Weissburger. B.P. 627,814.

**Organic Pigments and Moulding Powders.** Calico Printers' Assocn. Ltd., L. A. Lantz, A. Schofield, and E. Spinner. B.P. 630,359.

Insoluble azo pigments and moulding powders are obtained by treating a finely divided polyvinyl benzal prepared by the method of B.P. 582,019 (cf. J.S.D.C., 63, 278 (1947)) with an aqueous solution of an alkali metal salt of a coupling component, rinsing, then treating with an aqueous solution of a diazonium salt of an aromatic amine containing no water-solubilising groups, rinsing, and, if desired, hot-soaping the product. C. O. C.

**Substantive Metallisable Monoazo Pyrazolone Dyes.** J. R. Geigy A.-G. B.P. 629,412.

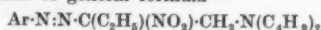
Mainly red substantive dyes which may be metallised (especially with copper compounds) in substance or on the fibre are made by coupling 1 mol. of 1-diazo-6-nitro-8-naphthol-4-sulphonic acid with 1 mol. of a dipyrazolone derivative of urea or thiourea of general formula—



(X = O or S; Y = methyl, ethyl, or phenyl; Z = a benzene-series radical combined in the 1:4-positions or a diphenyl-series radical combined in the 4:4'-positions). Thus 1-*p*-aminophenyl-3-methyl-5-pyrazolone is condensed with phosgene, and the resulting urea derivative coupled with 1-diazo-6-nitro-2-naphthol-4-sulphonic acid in presence of soda ash. The resulting monoazo compound dyes cellulose brown-orange, rendered redder and faster to water and light by aftercoupling. E. S.

**Azo Compounds from 1-Di-*n*-butylamino-2-nitrobutane.** E. F. Degering, G. van Biema, and Purdue Research Foundation. U.S.P. 2,474,779.

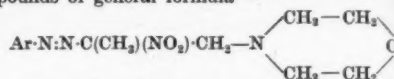
Compounds of general formula—



(Ar =  $\beta$ -naphthyl or *p*-chlorophenyl) prepared by coupling the diazotised aromatic amines with 1-di-*n*-butylamino-2-nitrobutane in acid solution, are useful orange or yellow dyes for silk, wool, and rayon. C. O. C.

**Azo Compounds from 1-*N*-morpholinyl-2-nitropropane.** E. F. Degering, G. van Biema, and Purdue Research Foundation. U.S.P. 2,474,780.

Compounds of general formula—



(Ar = aryl, nuclear-substituted aryl, or arylazoaryl), obtained by coupling 1-*N*-morpholinyl-2-nitropropane in acid or alkaline solution, are dyes for silk and wool, and in some cases for cotton and rayon. C. O. C.

**Substantive Disazo Dyes.** J. R. Geigy A.-G. B.P. 630,181.

Red substantive dyes are made by condensing 2 mol. of an aminoazo dye of general formula  $\text{R}^1\text{-N:N-R}^2\text{-NH}_2$  ( $\text{R}^1$  = the radical of an *O*-acyl-1-amino-8-naphthol-3:6- or -4:6-disulphonic acid;  $\text{R}^2$  = the radical of a primary aromatic amine coupling in the *para* position) with 1 mol. of an aromatic primary diamine by means of 2 mol. of phosgene, and subsequently hydrolysing the *O*-acyl groups. Thus, all parts being by weight, the monoazo dye (62:1) prepared by diazotising the *O*-*p*-toluenesulphonyl ester of 1-amino-8-naphthol-3:6-disulphonic acid and coupling with cresidine is dissolved together with 4:4'-diaminostilbene-2:2'-disulphonic acid (18:5) in water (800) by addition of soda ash. Phosgene is passed in until primary amine can no longer be detected, and the condensation product is filtered off, and saponified in dilute caustic alkali at 80–90°C. E. S.

**Disazo Chrome Dyes.** C. I. Anderson and Allied Chemical & Dye Corpn. U.S.P. 2,474,024.

Disazo chrome dyes of the type *o*-aminophenol → aminonaphtholsulphonic acid → acylacetarylide are more level dyeing than the similar dyes where the end component is a pyrazolone compound. The preferred end component is acetoacetanilide, but other compounds containing a reactive methylene group, e.g. acylacetic esters, amides, and nitriles and methylene diketones, can be used. The first diazo component may also be derived from an *o*-aminobenzoic acid; thus a range of hues, including green, olive, brown, grey, and black, can be produced on animal and polyamide fibres. Thus 4-nitro-2-aminophenol is diazotised and coupled under alkaline conditions with 1 mol. of 1-amino-8-naphthol-4-sulphonic acid, and the resulting aminoazo compound diazotised and coupled with 1 mol. of acetoacet-*o*-anisidine in presence of acetic acid. The product dyes wool dark brown, converted by afterchroming to olive green, fast to light and milling. E. S.

**Yellow Disazo Dyes for Imbibition Printing of Motion Picture Films.** Technicolor Motion Picture Corpn. B.P. 628,760.

**Substantive Disazo Dyes containing Copper.** J. A. Schedler, R. Whalley, and Clayton Aniline Co. Ltd. B.P. 628,028.

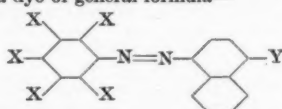
An alternative method of converting the disazo dyes derived from tetrazotised dianisidine described in B.P. 615,210 (J.S.D.C., 65, 303) into their copper complexes consists in using, instead of ammoniacal copper sulphate, other aqueous solutions containing  $\text{Cu}(\text{NH}_3)_4^+$  ions. Or, organic cupritetrammine compounds can be used, prepared by reaction of an organic base, e.g. methylamine, with a cupric salt or cupric hydroxide. E. S.

**Halogenated Naphthaquinone Derivatives—Dyes for Cellulose Acetate and Nylon.** Sandoz Ltd. B.P. 629,706.

Violet to red-blue dyes for cellulose acetate and nylon of good fastness to gas fumes, are made by halogenating aminohydroxy-1:4-naphthaquinoneimines and hydrolysing to the corresponding halogenated 5:8-dihydroxy-1:4-naphthaquinoneimines. The aminohydroxy-1:4-naphthaquinoneimines may be prepared by reducing 1:5-dinitronaphthalene with sulphur in fuming sulphuric acid. Thus a mixture of 1:5-dinitronaphthalene, sulphur, and 7% oleum is stirred at < 28°C. After reducing the acid strength by adding water with cooling, bromine is introduced with a small amount of iodine as catalyst, and the whole heated for 12–14 hr. at 80°C. Hydrolysis occurs during bromination, and the resulting dibromo-5:8-dihydroxy-1:4-naphthaquinoneimine is separated by pouring into ice and water and filtering. R. K. F.

**Dyes for Colouring Hydrophobic Substances soluble in Hydrocarbons.** Ciba Ltd. B.P. 628,598.

Fats, waxes, oils, resins, etc. soluble in hydrocarbons are coloured orange to brown by dissolving in them or in the solvent a dye of general formula—



(> 1 X = Hal, the other X's = H, Y = amino). The dyes are obtained by coupling a diazotised halogenoaniline containing > 1 halogen atom, e.g. 2:5-dichloroaniline, with 1-aminonaphthalene or an N-alkyl or N-aralkyl derivative thereof. C. O. C.

**Acid Treatment of Thionaphthen and Naphthacridine Vat Dyes.** J. F. Cullinan, L. D. Lytle, and American Cyanamid Co. U.S.P. 2,475,821.

Indigoid vat dyes having at least one thionaphthen nucleus are obtained very finely divided by forming them into a slurry with 20-40 parts of sulphuric acid of such strength that at the temp. of treatment not > 10% of the total dye is in solution at any one time, agitating until all the dye is converted into the insoluble sulphate, and then hydrolysing to reform the dye.

U.S.P. 2,475,847.

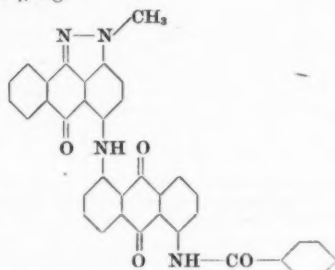
Naphthacridine and naphthacridone dyes are similarly treated. C. O. C.

**Benzanthrondicarboxyamides—Vat dyes.** Ciba Ltd. B.P. 628,566.

A benzanthrondicarboxylic acid, or a functional derivative of one, is condensed with an amine or a mixture of two different amines. The dicarboxylic acid or derivative used must be one which is incapable of forming an internal anhydride. The products are vat dyes and may be converted to the corresponding carbazole derivatives and/or halogenated to give other vat dyes. Thus benzanthrone-6:13-dicarboxylic acid is treated with thionyl chloride in dichlorobenzene to give the corresponding acid chloride. After distilling off excess thionyl chloride 1-amino-5-benzoylaminoanthraquinone is added, and the whole heated at 150°C. for 2 hr. The resulting yellow vat dye is filtered off and washed with ethanol. R. K. F.

**Vat Dyes from Pyrazoleanthrimide Derivatives.** Ciba Ltd. B.P. 627,078.

Orange to brown vat dyes are obtained by heating a compound of general formula  $R^1-NH-R^2$  ( $R^1$  = a pyrazoleanthrimide residue;  $R^2$  = an anthraquinone residue containing an acylamino group; the position of the NH group connecting the two residues is 5 with respect to either the 1:9-pyrazole ring in  $R^1$  or to the 1-acylamino group in  $R^2$ ), e.g.—



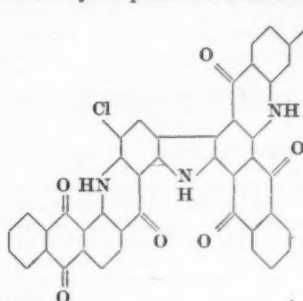
with an aluminium chloride condensing agent. R. K. F.

**Acridone-Anthrimides and -Carbazoles—Vat Dyes.**

General Aniline & Film Corp., F. Max, and D. I. Randell. B.P. 627,519.

An anthraquinone-2:1-N:1':2'-N-6'-halogenobenz-(or naphth)acridone having the 5' position free for subsequent ring closure is condensed with a 4-, 5-, or 8-aminoanthraquinone-2:1-N:1':2'-N-benzacridone to give a green to grey anthrimide vat dye. On ring-closing a red to blue carbazole vat dye is formed. Thus anthraquinone-2:1-N:1':2'-N-3':6'-dichlorobenzacridone and anthraquinone-2:1-N:1':2'-N-4-amino-4'-chlorobenzacridone are heated

for 3 hr. at 210°C. with sodium carbonate and copper acetate in molten naphthalene. The resulting product is separated by diluting the hot melt with chlorobenzene. The anthrimide so obtained is ring-closed by heating at 90-100°C. for 1 hr. with anhydrous aluminium chloride in nitrobenzene. After pouring into water, acidifying with hydrochloric acid, and steam-distilling off the nitrobenzene, the vat dye of probable constitution—



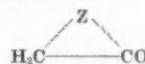
R. K. F.

**Cyanine Sensitising Dyes.** General Aniline & Film Corp. and A. W. Anish. B.P. 627,521.**Metal-containing Azomethine Dyes for Nylon.** General Aniline & Film Corp., H. W. Grimm, and H. B. Freyermuth. B.P. 629,473.

Yellow to purple neutral-dyeing dyes for nylon are prepared by treating the product of condensing an aromatic o-hydroxyamine and an o-hydroxybenzaldehyde with a bivalent cobalt salt. Alternatively the cobalt salt may be present during the condensation. Thus, 4-nitro-2-aminophenol is condensed with 5-nitrosalicylaldehyde by refluxing together in ethanol for 10 min. After pouring into conc. aqueous ammonia, a solution of cobaltous chloride is added, and the whole heated at 80-90°C. for 2 hr., cooled, and filtered. R. K. F.

**Polymethine Dyes and their Intermediates—Photographic Sensitisers or Desensitisers.** Kodak Ltd., F. M. Hamer, R. J. Rathbone, and B. S. Winton. B.P. 629,106; B.P. 629,122; B.P. 629,123.**Oxonole, Hemi-oxonole, and meroCyanine Dyes and their Intermediates.** Gevaert Photo-Producten N.V., A. E. Van Dormael, and T. H. Ghys. B.P. 628,837.

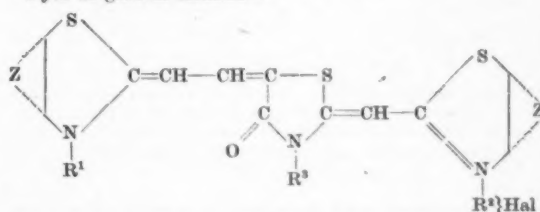
Treating a pyridinium salt having a labile N atom with compounds of formula—



(Z = the non-metallic atoms needed to complete a heterocyclic nucleus) in presence of a strong basic condensing agent yields either oxonole dyes or intermediates convertible into polymethine dyes by treatment with a compound containing a reactive cyclomethylene or reactive methyl group or with the methylene base corresponding to the latter. C. O. C.

**Rhodacarbocyanine Dyes.** T. R. Thompson and General Aniline & Film Corp. U.S.P. 2,475,163.

Dyes of general formula—



( $R^1$  and  $R^2$  = alkyl or aryl;  $R^3$  = alkyl, allyl, or aryl; Z = remainder of a benzene or naphthalene nucleus) are obtained by interaction in presence of acetanilide of 2 mol.



of quaternary salts of 2-methylbenzthiazoles or 2-methylnaphthothiazoles, 1 mol. of ethyl orthoformate, and 1 mol. of a rhodanine. C. O. C.

**Titanium Dioxide.** New Jersey Zinc Co., L. C. Copeland, and C. W. Farber. B.P. 629,333.

Rutile  $\text{TiO}_2$  is obtained by hydrolysing a  $\text{TiSO}_4$  solution containing < 0.025% of  $\text{P}_2\text{O}_5$  on the  $\text{TiO}_2$  present and calcining the precipitate at 900–975°C. for 1–2 hr.

C. O. C.

**Coloration of Paper.** V. G. Morgan and I.C.I. Ltd. (XI, p. 163.)

## V—PAINTS; ENAMELS; INKS

### PATENTS

**Producing Visible Records.** National Cash Register Co. B.P. 629,165.

Two substances which on mutual contact form a coloured compound, e.g. kaolin and 3:3-bis-*p*-dimethylaminophenylphthalide, are separately dispersed in a coating solution, e.g. of methyl cellulose or casein, and the two solutions mixed, applied to a base, and dried. On pressing on the dried film, e.g. by writing or typing, the binder between the dissimilar particles is ruptured and they are forced into contact with one another at the point of pressure, with resultant formation of colour. C. O. C.

**Multicoloured Relief Patterns on Wallpaper or other Surfaces.** K. L. M. Nielsen. B.P. 628,131.

A coating solution is used in which small liquid-absorbent particles coloured differently from the coating composition are dispersed. The coating solution or the dye used to colour the particles is such that the dye in the particles, even when dry, will penetrate the coating composition as long as the latter is wet. C. O. C.

**Transparent Coating Compositions.** Du Pont. B.P. 630,334.

Transparent brown and black finishes of good durability and colour stability are obtained by using a composition comprising an organic-film forming vehicle containing a cellulose ester or ether and a hydrous iron oxide pigment of average particle size approx. 30  $\mu$ . Addition of aluminium powder to the brown compositions gives finishes resembling gold or bronze powder coatings, and addition to the black compositions yields a metallic finish which cannot be obtained by previously known methods. C. O. C.

## VI—FIBRES; YARNS; FABRICS

**Relationship between the Average End-point Distance and Chain Length in Fibre Molecules.**

G. Porod. *Sitzungsber. Öster. Akad. Wiss.*, 158, (2), 251–255 (1949).

The statistical treatment of this problem by Kuhn (*Kolloid Z.*, 68, 2 (1934)) and the exact formula of Eyring (*Phys. Rev.*, 39, 746 (1932)) are briefly discussed. A method is then derived for continuous flexible fibres, which replaces the two constants of the Eyring formula by one, and gives a simpler relation between the mean square of end-point distance and chain length. H. H. H.

**Water Sorption and the Polyphase Structure of Cellulose Fibres.** J. A. Howsmon. *Text. Research J.*, 19, 152–162 (March 1949).

Using a modified equilibrium moisture regain method, the sorption capacity of a wide variety of cellulosic materials has been measured. The data have been used to place the materials in a revised order of accessibility, and a correction has been advanced to compensate for the differences between accessibilities to water of native and regenerated crystals. It is considered that the accessibility of crystals and/or crystal size may be as large a factor in determining different reactivities of various celluloses as are differences in total crystalline content. Recrystallisation has been shown to be a determining factor in acid hydrolysis studies of cellulose at high temperatures, probably leading to high estimates of degree of crystallinity. P. C.

**Small-angle X-ray Scattering in Various Cellulose Fibres and its relation to the Micellar Structure.** A. N. J. Heyn. *Text. Research J.*, 19, 163–172 (March 1949).

**Absorption and Fixation of Sodium Hydroxide by Mercerised Cellulose.** A. Bréquet, R. Viatte, and C. Chareyron. *Compt. rend.*, 228, 1499–1501 (1949); *Chem. Abs.*, 43, 7233 (25th Sept. 1949).

The swelling of mercerised cellulose in NaOH soln. plotted against the NaOH concn. does not give a curve of three zones as is the case with native cellulose. Mercerised cellulose swollen in 0–35% NaOH by vol., then pressed, washed, neutralised, rewashed, and dried, swells again in a weaker NaOH soln. as if it had not undergone the previous treatment. The maximum absorption of NaOH corresponds to  $(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{NaOH}$ . C. O. C.

**Damage to Wool on Discharging with Rongalite.** E. Elöd and H. Zahn. *Textil Praxis*, 4, 27–30 (Jan. 1949).

The literature is reviewed dealing with the action of reducing agents, especially Rongalite, on wool and other keratin fibres and with attempts made to stabilise wool against damage by Rongalite. A method proposed to overcome this defect involves treatment with dibromomethane, and its efficiency is confirmed by assessment of alkali solubility and supercontraction in various media. B. K.

**Measurement of Friction between Single Fibres. II—Frictional Properties of Wool Fibres measured by the Fibre-twist Method.** J. Lindberg and N. Gralén. *Text. Research J.*, 19, 97–99 (Feb. 1949).

Comments are made by K. R. Makinson on this paper and are answered by the authors. Some new data are reported. P. C.

**Allwörden's Reaction.** J. Lindberg. *Text. Research J.*, 19, 43–45 (Jan. 1949).

The author concludes from a study of Allwörden's reaction, aided by electron photomicrographs, that wool possesses a surface skin about 100Å. thick of very dense, homogeneous, and structureless material. The skin appears to be comparatively firmly fixed to the fibre at or under the scale edges. The function of this skin in the reactions used to determine the cause of damage of wool fibres is discussed. P. C.

**Absorption of Caustic Soda and Basic Dyes by Wool, Silk, and Polyamides.** E. Elöd and H. G. Fröhlich. *Melliand Textilber.*, 30, 405–410 (Sept. 1949).

The authors' investigation shows that wool and silk behave similarly as regards action of caustic soda. Absorption begins at pH 7, increases slowly, then shows rapid increase at pH 11.5 and saturation at pH 13–13.5. The uptake of basic dyes passes through a maximum. Polyamides appear to react with caustic soda or basic dyes in a similar manner to protein fibres. B. K.

**Spectrographic Proof of Diketopiperazines in Silk Fibroin.** J. O. Fixl and E. Schauenstein. *Sitzungsber. Öster. Akad. Wiss.*, 158, (1), 146–148 (1949).

Whereas cold 0.5% aqueous NaOH at room temperature produces no effect on the spectrum of fibroin films, which is identical with that of tyrosine at pH 9.2, this changes at 60–70°C. and pH 13 to that of glycyltyrosine anhydride. The presence of the diketopiperazine ring is confirmed by the characteristic pH dependence of the absorption spectrum of glycyltyrosine anhydride. H. H. H.

**Directional Dependence of Ultra-violet Absorption and Chromophores in Highly Oriented Silk Fibroin.** E. Schauenstein, J. O. Fixl, and O. Kratky. *Sitzungsber. Öster. Akad. Wiss.*, 158, (1), 143–146 (1949).

Highly oriented silk fibroin films possess a double directional dependence of light absorption produced—(1) by the anisotropic absorption of the tyrosine chromophore caused by tension and manipulation, and (2) by the occurrence of a new absorption within a zone at a definite angle to the chain axis. H. H. H.

**Experimental and Theoretical Study of the Absorption and Swelling Isotherms of Human Hair in Water Vapour.** H. J. White Jr. and P. B. Stam. *Text. Research J.*, 19, 136–151 (March 1949).

Measurements have been made of the length and diameter changes of human hair accompanying the adsorption of water, and the effect of small loads on these changes



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has been studied. The results can be accounted for semi-quantitatively by a theory developed in detail in the paper.

P. C.

**Interpretation of the Mechanical Behaviour of Rayon.** L. Hermance. *Text. Research J.*, 19, 61-72 (Feb. 1949).

A working hypothesis is put forward to explain the mechanical behaviour of rayon based on observations made by the author but not reported in the present paper. Some new points of view are expressed.

P. C.

**Interaction of Various Organic Liquids with Cellulose Acetate Fibres as detected by Specific Gravity Measurements.** F. Fortess. *Text. Research J.*, 19, 23-35 (Jan. 1949).

The pycnometer technique of determining specific gravity of solids has been used to study the rate and degree of penetration of a wide variety of organic liquids into cellulose acetate yarn. The rate of attainment and magnitude of the values for apparent specific gravity were a function of the size and shape of the hydrocarbon portion of the penetrating molecule as well as of the donor or acceptor properties of the polar groups. The method distinguishes between penetrating and non-penetrating liquids. Useful information is obtained by comparing the data for various members of a homologous series. The results are discussed in relation to the molecular structure of the compounds and their carbon chain length. A theory is advanced to explain how molecules penetrate and solvate cellulose acetate, and applications of this technique are indicated.

P. C.

**Contraction of Polyamide Fibres in Phenol.** E. Elöd and H. Zahn. *Melliand Textilber.*, 30, 349-350 (Aug. 1949).

The behaviour of a number of commercial brands of polyamide rayons and polyurethane rayon in dilute aqueous solutions of phenol at ordinary temperature was investigated, and it was found that lateral contraction increases with the concentration of the phenol solution. There are noticeable differences between individual polyamides, and these may be used for their characterisation.

B. K.

**$\alpha$ - $\beta$ -Transformation in a Polypeptide.** C. H. Bamford, W. E. Hanby, and F. Happey. *Nature*, 164, 751-752 (29th Oct. 1949).

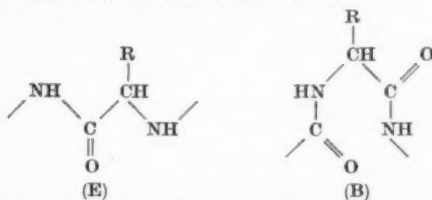
It is reported that the copolymer of  $\gamma$ -methyl L-glutamate with DL- $\beta$ -phenylalanine can be spun in two forms ( $\alpha$  and  $\beta$ ), and that  $\beta$  is obtained when solutions of the copolymer in formic acid are extruded into non-solvents or precipitated from formic acid solutions. X-Ray photographs are included of the two modifications. Immersion of disoriented  $\beta$ -fibres in *m*-cresol for 5 min. led to partial reversion to  $\alpha$ , which was found to be oriented. It is concluded from various data that the configuration of the polypeptide is decisively influenced by the solvent. Accumulated evidence suggests that the ability to produce a  $\beta$ -configuration is not primarily a function of the acid strength of the solvent, but is connected with the small molecular volume of formic acid.

H. H. H.

**Stable Configurations of a Polypeptide Chain.**

S. Mizushima, T. Simanouti, M. Tsuboi, T. Sugita, and E. Kato. *Nature*, 164, 918-919 (26th Nov. 1949).

The model proposed by Ambrose *et al.* (*Nature*, 163, 483 and 859 (1949)) for the molecular structure of  $\alpha$ -keratin has already been presented by two of the authors (*Kagaku*, 17, 24 and 52 (1947), and 18, 452 (1948)) based on the energy consideration for the intramolecular rotation. Using symbols E for the extended form of the polypeptide chain and B for the bent or folded form,



it is shown how to construct various stable configurations by suitable combinations of E and B, taking into account the fact that all the amino residues of the chain are of the

L-form. Various experimental results obtained for proteins are also explained from the above molecular configurations. Evidence is submitted for the existence of the B-form of the molecule of acetylglycineanilide and hence for certain amino-acid residues in the polypeptide chain.

H. H. H.

**Transmittance, Reflectance, and Absorbance of Near Infra-red Radiation in Textile Materials.**

R. H. Wilhelm and J. B. Smith. *Text. Research J.*, 19, 73-88 (Feb. 1949).

The transmission of infra-red radiation through layers of textile fabrics has been studied, and a theory developed which describes adequately the experimental data. Reflectance and absorbance values can also be estimated. Measurements have been made on cotton, viscose and cellulose acetate rayons, and woollen and worsted fabrics, in which such variables as the nature of the fibre thickness in the textile pile, weight and construction of fabric, moisture content, and presence of dyes have been studied. Whilst the nature of the fibre affects transmittance, the fabric construction does not, the important variable being the number of fibres in the path of illumination. Transmittance increases to a maximum and then falls as moisture content is increased. Dyes markedly affect transmittance, which is decreased greatly by the presence of a sulphur black dye.

P. C.

#### PATENTS

**Alginate Threads.** Courtaulds Ltd., E. E. Tallis, and H. R. S. Clotworthy. *B.P.* 627,151.

The viscosity of aqueous alkali alginate solutions used in the production of alginate threads can be controlled by addition of sodium hydrosulphite.

W. G. C.

**Spinning Collagen Solutions.** A. Cresswell and American Cyanamid Co. *U.S.P.* 2,475,129.

Collagen is dissolved in an aqueous organic acid, and the solution filtered and then extruded through a spinneret coated with a basic nitrogen compound containing a long-chain alkyl radical of  $> 11$  C into an alkaline aqueous solution of ammonium and/or sodium and/or zinc and/or magnesium sulphate. The coating prevents clogging of the spinneret.

C. O. C.

**Polyvinyl Chloride Filaments.** D. Finlayson and A. W. M. Cooke. *B.P.* 627,426.

Filaments and films of polyvinyl chloride, which is insoluble in methyl ethyl ketone, are formed by evaporating solutions made by wetting the polyvinyl chloride with acetone, refluxing in a mixture of a cyclic compound, e.g. cyclohexanone, and a volatile non-solvent, e.g. methyl ethyl ketone, and diluting the hot solution with the non-solvent till the ratio of diluent : solvent is  $> 8 : 1$ .

W. G. C.

**Retarding the Crystallisation of Synthetic Linear Polyamides.** I. F. Walker and Du Pont.

*U.S.P.* 2,473,924.

1-5% by weight of a compound of general formula  $R^1\text{-CO-X-R}^2\text{-SO}_3\text{M}$  ( $R^1$  = an open-chain univalent hydrocarbon radical of 11-19 C; X = O,  $\text{N}(\text{CH}_3)$ , or  $\text{N}(\text{C}_2\text{H}_5)$ ;  $R^2$  = a bivalent hydrocarbon radical of 1-6 C; M = Na or K), e.g. sodium 2-oleoyloxyethanesulphonate, is incorporated.

C. O. C.

**Fractionation of Linear Polyamides.** G. B. Taylor and Du Pont. *U.S.P.* 2,473,920.

Polyamides can be fractionated by partly precipitating the polymers from the solution by successive additions of non-solvents.

C. O. C.

**Coated Nylon Thread.** S.p.A. Lavorazione Materie Plastiche. *B.P.* 628,466.

A coating of polyvinyl chloride on nylon thread protects it against friction and atmospheric agents.

W. G. C.

**Aminocarboxyamides.** Algemeene Kunstzijde Unie N.V. *B.P.* 627,596.

Fibre-forming polyamides are obtained by heating an aminocarboxyamide, e.g.  $\epsilon$ -aminocaproamide, with at least its own weight of water, removing the water, and completing the reaction by further heating.

W. G. C.

**Linear Polyamides.** Wingfoot Corp'n. *B.P.* 627,733.

Polyamides which form fibres with reduced plastic flow are obtained by treating an arylenedicarboxylic acid or a derivative thereof of formula  $R^1\text{-CH}_2\text{-CH}_2\text{-R}^2\text{-CH}_2\text{-CH}_2\text{-R}^1$  ( $R^1$  =  $-\text{COOH}$ ,  $-\text{CO-NH}_2$ ,  $-\text{CO-Cl}$ , or  $-\text{CN}$ ;  $R^2$  = an

arylene radical) with an aliphatic diamine, e.g. *p*-phenylenedipropionic acid and decamethylenediamine.

W. G. C.

**Natural and Synthetic Rubber Fibres.** N.V. De Bataafsche Petroleum Maatschappij. *B.P.* 627,209.

Fibres of improved strength are made by extruding a natural or synthetic polymer of a conjugated diene, stretching, and then treating with sulphur dioxide or sulphurous acid.

B.P. 627,210.

Fibres of good tensile strength are also obtained by spinning a solution of the polydiene into a coagulating bath containing sulphur dioxide, stretching while swollen, and finally drying while stretched.

W. G. C.

**Pulverising Fibres.** Société Internationale Soie-Cosmétique. *B.P.* 628,784.

Animal, vegetable, or synthetic fibres are readily disintegrated mechanically, e.g. in ball or roller mills, if they are first treated with an oxidising agent under conditions preserving their fibrous structure.

C. O. C.

## VII—DESIZING; SCOURING; CARBONISING; BLEACHING

**Application of Carboxymethyl Celluloses in Desizing.** G. Ulrici. *Teintex*, 14, 463-477 (Nov. 1949).

The chemistry of carboxymethyl celluloses is discussed. Experiments have been carried out to observe the desizing action of carboxymethyl celluloses on wool and cotton under various conditions together with estimations of extension and tensile strengths of the treated materials, which would indicate such treatments to be of interest to the textile processor.

B. K.

**Scouring and Detergents.** W. Kling. *Melliand Textilber.*, 30, 412-419 (Sept. 1949).

A critical review of the literature, with 39 references, dealing with physicochemical aspects of the behaviour of synthetic detergents in aqueous solutions and its significance in subsequent scouring efficiency.

B. K.

**Wool Scouring.** R. Gutensohn. *Textil-Praxis*, 4, 562-565 (Nov. 1949).

Old and new methods of wool scouring are discussed with special reference to the pH of the scouring liquors and any damage to the wool fibre.

B. K.

### PATENT

**Stabilising Peroxide-bleached Cellulose Esters.** W. M. Gearhart, T. S. Gardner, and Eastman Kodak Co. *U.S.P.* 2,475,953.

Incorporation of an unsaturated organic compound, particularly an organic ester, e.g. styrene or an allylate, confers stability to discoloration on heating for 1 hr. at 205°C.

C. O. C.

**Bleaching Mildewed Poplar Groundwood.** K. A. Craig and Paper Patents Co. (XI, p. 163.)

**Fastness to Washing of Coloured Textiles.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25. (XIV, p. 166.)

**Fastness of Dyeings to Carbonising.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25. (XIV, p. 166.)

## VIII—DYEING

**Dyeing of Polyamides.** J.-P. Niederhauser. *Textil-Rund.*, 4, 400-405 (Nov. 1949).

The constitution of polyamide fibres, nylon and Irganides, is discussed, and the dyeing of such fibres considered theoretically. The dyeing of acid dyes is considered in detail with regard to the fixation of dyes by the fibre under different pH conditions and times of dyeing.

B. K.

**Turkey Red Dyeing.** R. Haller. *Melliand Textilber.*, 30, 410-411 (Sept. 1949).

An investigation into the action of polymers of ricinoleic acid in the presence of metallic salts and also of tannic acid in the production of Turkey Red.

B. K.

**Naphthol Dyeing and Printing.** R. H. Nuttall. *Amer. Dyestuff Rep.*, 38, P232-P233 (7th March 1949).

Practical details and typical recipes are given for the application of azoic dyes to cotton in the form of raw

stock, yarn packages, hosiery, and piece goods, and in printing.

W. K. R.

**Contribution of Solvation to Stability of Anthraquinone Vat Dye Suspensions. Evaluation and Correlation with the Phenomenon of Migration.** D. P. Graham and A. F. Benning. *J. Phys. Colloid Chem.*, 53, 846-860 (1949); *Chem. Abs.*, 43, 7232 (25th Sept. 1949).

The stability of dye suspensions to precipitation was studied as an explanation for migration of dyes in dyeing fabrics. A "solvation ratio" *S* was selected as the ratio of ionic concentration *I* of an electrolyte required for incipient flocculation to that calculated *I*<sub>0</sub> to produce the same effect upon a hypothetical unsolvated suspension at the same  $\zeta$ -potential. The expression derived for the latter case was  $\zeta^2 = 1.74 \times 10^4 \times \sqrt{I}$ . For fourteen dyes examined, *S* was 8-130 for NaCl, with corresponding severity of migration.

C. O. C.

**Stability of Vat Colours at Elevated Temperatures.** American Association of Textile Chemists and Colorists, Piedmont Section. *Amer. Dyestuff Rep.*, 38, P213-P231, P239 (7th March 1949).

The reduced solutions of many vat dyes, e.g. Blue BCS type, decompose or change hue at the high temperatures (> 180°F.) used in modern continuous dyeing operations. It has been found that the addition of dextrin of high alkali-labile number (a measure of the amount of dextrin attacked by alkali under specified conditions) to the reducing bath (1-3 oz./gal. (U.S.A.)) stabilises sensitive dyes to over-reduction and enables the true shade and colour value to be obtained. Dextrins of low alkali-labile number, however, and starches, sugars, gelatin, glue, etc. possess no protective properties. A dyebath that has decomposed by over-reduction may be partly restored to produce satisfactory dyeing by the addition of a suitable dextrin, and change in hue in re-reducing and stripping vat dyeings is similarly prevented. Plant-scale trials in which various sensitive vat dyes were applied at high temperature by a number of different methods confirmed the effectiveness of dextrin as a stabiliser.

W. K. R.

**Control of Factors influencing Shade in Some Mills manufacturing 20-oz. Olive Drab Suiting and 32-oz. Olive Drab Overcoating.** L. D. C. Ward. *ORR* 274/49\* (PB 86,253).

The preparatory, finishing, and dyeing procedures at 11 American firms showed significant lack of control of each operation within each mill as well as lack of uniformity of operation and technique in the processing cycle from mill to mill. Suggested methods of improvement are given.

C. O. C.

\* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see J.S.D.C., 66, 53 (Jan. 1950).

### PATENTS

**Dyeing of Nylon with Insoluble Acetate Rayon Dyes followed by Steaming.** C. M. Croft and Celanese Corp. of America. *U.S.P.* 2,474,890.

Steaming the dyed nylon for 3-7 min. at 225-235°F. at 4-8 lb./sq. in. pressure gives heavier dyeings of improved fastness to washing, and is particularly effective with the red dyeings given by 1-hydroxy-4-aminoanthraquinone and 1-hydroxy-4-amino-6-bromophenylazodioxymethyl-*m*-chloroaniline respectively.

C. O. C.

**Rendering Dyed Acetate Rayon Fast to Gas Fading.** R. J. Mann, H. C. Olpin, and British Celanese Ltd.

B.P. 628,022.

The material is treated with a water-soluble condensate of an aldehyde, an alcohol, and an aminotriazine containing > 1 H attached to amino N and then rendering the condensate water-insoluble. Thus acetate rayon dyed blue with 0.5% of its weight of 1-methylamino-4- $\beta$ -hydroxyethylaminoanthraquinone is impregnated with its own weight of a liquid obtained by diluting 140 parts of the following condensate with 10,000 parts of water. The condensate is made by heating under reflux on a water-bath 126 g. of melamine, 540 c.c. of 37% formaldehyde, and 500 c.c. of methylated spirit, continuing to heat for 15-30 min. after a homogeneous solution is obtained, and finally cooling and diluting to a weight 10 times that of the melamine used with water or methylated spirit. After impregnation the fabric is dried and then steamed for

15–30 min. with saturated steam at 104–5°C. The protection given against gas fading resists laundering.

C. O. C.

**Colouring Highly Polymeric Linear Esters.** R. Hardwick, E. Waters, and I.C.I. Ltd. *B.P.* 629,452. Terylene is dyed by treatment with a primary aromatic amine and a coupling component, followed by diazotisation and coupling *in situ*.

C. O. C.

**Absorption of Caustic Soda and Basic Dyes by Wool, Silk, and Polyamides.** E. Elöd and H. G. Fröhlich. (VI, p. 158.)

## IX—PRINTING

### PATENTS

**Printing Difficultly Oxidisable Sulphuric Ester Salts of Leuco Vat Dyes using Dichromate-Acid Vapour Development.** W. B. Hardy, E. M. Hardy, and American Cyanamid Co. *U.S.P.* 2,474,785.

Full development is quickly obtained by adding an alkyl- or alkenylanilinesulphonic acid or a water-soluble salt thereof to the printing paste. Thus, all parts being by weight, the sodium salt of leuco-tetrabromindigodisulphuric ester (7) is mixed with sodium 2-amino-3:5-dimethylbenzenesulphonate (2) and sucrose (1.1). A paste containing the above mixture (3), urea (6), mixture of 40% acetamide, 40% diethylene glycol, and 20% furfuryl alcohol (3), water (11), 15% aqueous gum paste (70), ammonium chloride (0.75), 25% ammonia (2), and sodium dichromate (5) is printed on cloth. It completely develops to full colour value in 1–3 min. in formic and acetic acid vapours, compared with only 10–15% of full colour value after 10 min. ageing in absence of *m*-xyldine-sulphonic acid.

C. O. C.

**Photoprinting Diazotype Layers and Making Transition Prints.** General & Aniline Film Corp., W. H. V. Glahn, and L. N. Stanley. *B.P.* 628,914.

A diazotype light-sensitive layer contains a light-sensitive diazo compound and as coupling component an *o*-, *m*-, or *p*-hydroxyphenylthiourea which is unsubstituted in at least one of the positions *ortho* or *para* to the hydroxyl group.

C. O. C.

**Positive Diazotype and Negative Metal Reproduction Images.** General Aniline & Film Corp.

*B.P.* 629,656.

**Control of Contrast in Diazotype Materials.** General Aniline & Film Corp., C. Botkin, and S. C. Slikin.

*B.P.* 629,024.

Ascorbic or isoascorbic acid is incorporated in diazotype coating compositions to allow control of contrast.

C. O. C.

**Colour Photography.** Du Pont. *B.P.* 629,631. Bipack photographic films, one film element of which records two different colour separation records, and obtaining individual colour separation records therefrom are described.

C. O. C.

**Sulphite Anti-stain Bath for Multilayer Colour Film.** H. C. Harsh, J. E. Bates, and General Aniline & Film Corp. *U.S.P.* 2,475,134.

Staining of indophenol and azomethine dye images is prevented by treating them with an aqueous alkali-metal sulphite after processing but before drying.

C. O. C.

**Relief Images in Colour Photography.** Technicolor Motion Picture Corp. *B.P.* 628,847.

**Colour Rendering in Subtractive Colour Photography.** Kodak Ltd., R. M. Evans, and W. T. Hanson. *B.P.* 627,467.

**Tripack Material for Colour-photographic Printing on Opaque Supports.** G. B. Harrison and Ilford Ltd. *B.P.* 626,725.

**Colour-photographic Positives from a Single-emulsion Film.** P. A. L. Danlos and R. F. Daubigny-Ciriez. *B.P.* 627,547.

**Silk-screen Printing Paste for Gold Transfers for Ceramics.** Johnson Matthey & Co. Ltd., F. E. Kerridge, and C. S. Couper. *B.P.* 628,504.

Two parts of a mixture of gold powder, mercuric aurate, and a low-fusing flux together with 1–4 parts of a solution of a cellulose derivative are used.

C. O. C.

**Naphthol Dyeing and Printing.** R. H. Nuttall. (VIII, p. 160.)

**Control of Factors influencing Shade in Some Mills manufacturing 20-oz. Olive Drab Suiting and 32-oz. Olive Drab Overcoating.** L. D. C. Ward. (VIII, p. 160.)

**Figured Effects.** Bleachers' Assn. Ltd., F. Farrington, A. E. Stubbs, and E. Hall. (X, p. 163.)

## X—SIZING AND FINISHING

**Theory of the Kinetics of the Drying of Colloidal Capillary-porous Bodies.** A. V. Lykov. *Kolloid. zhur.*, 10, 289–304 (1948); *Chem. Abs.*, 43, 7272 (10th Oct. 1949).

The mathematics of drying porous bodies such as textiles is developed in 44 equations. The curve "rate of drying against percentage moisture in the material" shows two critical points, the first of which indicates that the zone of evaporation starts moving inside the material or that the surface water ceases to have the vapour pressure of saturated water, while the second corresponds to the boundary between the capillary and adsorbed moisture.

C. O. C.

**Function of Methylated Melamine-Formaldehyde Resin in controlling Shrinkage of Woollens.** C. R. Stock and D. J. Salley. *Text. Research J.*, 19, 41–43 (Jan. 1949).

Experiments have been made to determine the function of methylated melamine-formaldehyde resin as a shrink-proofing agent for woollens. No alteration in load-elongation hysteresis of fibres after treatment was noted, and there was no change in the frictional properties of fibres withdrawn from treated cloths. Tensile strength tests on detwisted treated and untreated yarns gave positive evidence that the resin caused the formation of a network of bonded fibres which inhibited shrinkage.

P. C.

**Kinetics of the Heterogeneous Reaction between Potassium Permanganate and Wool.** P. Alexander and R. F. Hudson. *J. Phys. Colloid Chem.*, 53, 733–752 (1949); *Chem. Abs.*, 43, 6896 (25th Sept. 1949).

The action between potassium permanganate and wool was studied at pH 2.0 and 9.2, at 0°C., in initial concentrations of permanganate of < 1%. In acid < 0.25% solutions the rate of removal of permanganate can be expressed as—

$$k_1 = \frac{1}{At} \ln \frac{a}{a-x}$$

( $A$  = wt. of wool in a given vol. of soln.,  $x$  = amount of  $\text{KMnO}_4$  reacted in time  $t$ ,  $a$  = amount of  $\text{KMnO}_4$  in the soln. at the start). Here the rate-determining step is a solution diffusion process across a liquid barrier at the surface of the fibre. In 0.25–1.0% soln. the relation is—

$$k_2 = \frac{a^n}{t} \ln \frac{a}{a-x}$$

( $n = 1.2-2.0$ ), inversely related to the wt. of wool. In this case,  $a^n$  represents a retardation effect due to deposition of  $\text{MnO}_2$  on the surface of the fibre. This deposit, which is probably attached to the amino groups of the side-chains of the keratin, can be removed only by treatment with  $\text{NaHSO}_4$  or  $\text{H}_2\text{O}_2$ , whereupon the rate of reaction with  $\text{KMnO}_4$  is restored.

C. O. C.

**Treatment of Nylon Webbing to increase Resistance to Abrasion.** C. A. Willis. *CADO* (Central Air Documents Office, Navy-Air Force) *Tech. Data Digest*, 14 (15), 25–25 (1949); *Chem. Abs.*, 43, 8142 (1949).

Samples of webbing were treated with aqueous dispersions of polyvinylbutyral resin and dried at 240–260°F. to remove all moisture and allow the resin to form a smooth film. Tests on a modified cable-and-pulley fatigue tester showed that webbing made from 240/12 nylon yarn has improved resistance to abrasion and ultra-violet radiation degradation compared with that made from 210/34 nylon yarn. Webbing treated with Merlon BN (an aqueous dispersion of polyvinylbutyral) lost 4–10% in breaking strength after 5000 abrading strokes, while untreated webbing lost 15–29%. Take-up of 4.5–6.5% resin was optimum for increasing abrasion resistance while retaining maximum flexibility. The treatment does not increase danger of slippage in standard parachute hardware.



Increase in twist of 2-4 t.p.in. in the yarn increased resistance to abrasion but lowered the ultimate breaking strength. Ageing at 120° F. for 500 hr. had little effect on the breaking strength of either treated or untreated yarn. Ageing at 100° F. and 95% R.H. for 600 hr. had little or no effect on breaking strength of either treated or untreated webbing. Degradation by ultra-violet radiation was decreased by dyeing the webbing olive drab with acetate rayon dyes. The plasticiser used for the resin was susceptible to micro-organisms; however, any fungi that appear on the untreated webbing do not affect its breaking strength and can be wiped off with a damp cloth.

C. O. C.

**Adhesion of Rubber and Textiles.** E. M. Borroff and W. C. Wake. *Trans. Inst. Rubber Ind.*, 25, 190-221 (Oct. 1949).

## II—Factors influencing the Load required to strip Rubber from Fabric and Foil Surfaces.

Experiments with chemically treated fabrics in which the mechanical factor was left unchanged and other experiments with foils showed the part played by specific factors in rubber-fabric adhesion to be relatively unimportant. Specific factors do exist, and their magnitude is connected with the existence of polar groups or groups that can be polarised. The adhesion secured by use of spun-rayon fabrics effectively outweighs all other factors.

## III—Examination of Test Technique.

The variation with the rate of stripping of the load needed to break rubber-fabric bonds is discussed for unvulcanised and vulcanised rubbers, and this is followed by discussion of the load variation with period of vulcanisation. The two features apparent in stripping tests are separated, and a simple direct tension test is suggested as a more reliable measure of adhesion. An improved stripping test is described, and this, together with the direct tension test, is discussed in a final section on the relation between the two tests and their application to practical problems.

## IV—Function of Staple Fibre in Rubber to Fabric Adhesion.

Investigation of the adhesion of rubber to a series of fabrics woven from spun and filament viscose and acetate rayons and nylon using the direct tension test showed that adhesion strength is a property of the staple fibre and is directly related to its tensile strength. The number of projecting fibres was determined and compared with the broken-off fibres recovered from a natural rubber cement stripped from a fabric. Size distribution histograms of the recovered fibres are given and discussed. Recommendations are made for utilising the results so far obtained in this investigation for producing improved rubber-textile goods.

C. O. C.

## PATENTS

**Anti-static Textiles.** General Aniline & Film Corp. and A. L. Fox. B.P. 629,659.

Textiles are prevented from accumulating electrical charges by treating them with a mixture of 99-90% of a textile lubricating oil and 1-10% of a dialkyl orthophosphate, one alkyl group being of 6-18 C and the other of 1-4 C, e.g. lauryl ethyl acid orthophosphate, so as to leave 0.1-10% by weight of the phosphate in the textiles.

C. O. C.

**Sizing or Finishing Yarns or Fabrics.** Monsanto Chemical Co. B.P. 628,754.

The material is treated with an aqueous solution or dispersion of formaldehyde or a water-soluble compound yielding formaldehyde on heating and an ammonium or amine salt of the copolymer of a styrene or substituted styrene and maleic anhydride or partial ester of maleic acid. 2-15% by weight of the salt is deposited in the material and there should be 1-20% formaldehyde on the weight of the salt. The treated material is dried at a high temperature to form an insoluble resin in it. The sized or finished material has a stiff finish, which resists washing; thus fabrics woven from a warp sized by this method have a stiff finish without further treatment after weaving.

C. O. C.

**Sizing or Finishing Textiles.** Monsanto Chemical Co.

B.P. 628,881.

The materials are treated with an aqueous solution or dispersion of an ammonium or amine salt of a copolymer of a styrene or substituted styrene and maleic anhydride

or a partial ester of maleic acid together with an unpolymerised urea-, thiourea-, melamine-, or dicyandiamide-formaldehyde condensate or an alkyl ether derivative of such a condensate or an unpolymerised aldehyde-phenol condensate. They are then dried and the resin is cured. A permanent stiff finish is obtained which is little affected by washing. Fabrics woven from warps so treated require no finishing on leaving the loom.

B.P. 629,097.

An aqueous solution or dispersion of an aliphatic polyamine and an ammonium or amine salt of a copolymer of styrene or a substituted styrene with maleic anhydride or a partial ester of maleic acid is used.

C. O. C.

**Treating Cellulosic Materials with Solvent Swelling Agents.** W. Watkins. B.P. 598,556.

This specification has been amended, but not so as to affect the abstract previously published (J.S.D.C., 64, 265 (1948)).

C. O. C.

**Treating Cellulosic Textiles with a Strong Hydroxide and Acrylonitrile.** J. W. Stallings and Röhms & Haas Co. U.S.P. 2,473,308.

Cellulosic textiles are given decreased moisture regain, decreased water absorbency, increased tensile strength, increased abrasion resistance, increased stiffness, altered dyeing properties, and high resistance to mildew by impregnating them with their own wt. of a 10-30% aqueous solution of a strong hydroxide at 0-30°C. and then treating them for 1-24 hr. at 0-35°C. in a 5-10% solution of acrylonitrile dissolved in an inert water-immiscible organic solvent.

C. O. C.

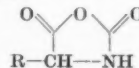
**Surgical Dressings.** L. Doub and Parke Davis & Co. U.S.P. 2,474,306.

Highly lyophilic and germicidal surgical dressings are obtained by treating a partly oxidised cellulose (carboxyl content 2-23%) with a high-mol. wt. quaternary ammonium salt, e.g. *p*-tert.-octylphenoxyethoxyethyl-dimethylbenzylammonium chloride monohydrate.

C. O. C.

**Reducing the Felting Properties of Wool.** Wolsey Ltd., J. L. Bailey, and P. Alexander. B.P. 627,910.

The tendency of wool to shrink is reduced by treating it in an aqueous liquid buffered at pH 5.5-11.0, drying it, and then treating with anhydrocarboxyglycine dissolved in an organic solvent. If desired the treatment may be carried out in presence of other fibres and/or a compound of general formula—

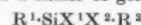


(R = a hydrocarbon chain! of > 7 C), e.g. octyldiketoxazolidine, may be incorporated with the anhydrocarboxyglycine to act as a softening agent.

C. O. C.

**Reducing the Felting Power and Increasing the Resistance to Abrasion of Wool.** Wolsey Ltd., P. Alexander, and C. Earland. B.P. 629,329.

Wool, if desired in presence of other fibres, is treated at 10-30% regain so as to coat its surface with 1.5-4.0% of its weight of the solid polymer produced by hydrolysing a mixture of  $\text{SiCl}_4$  and a silane of general formula



( $\text{R}^1$  and  $\text{R}^2$  = alkyl or aryl,  $\text{X}^1$  and  $\text{X}^2$  = Cl or Br).

C. O. C.

**Rendering Wool Fabrics Non-shrinking.** Monsanto Chemical Co. B.P. 628,605.

The laundry shrinkage of wool fabrics is reduced to zero without affecting their handle by applying to them 8-16% (on their dry weight) of a water-soluble melamine-aldehyde condensate or its alkyl ether, curing, and finally moistening the fabric and allowing it to relax.

C. O. C.

**Delustering Copolymer Filaments.** J. E. Snyder and Wingfoot Corp. U.S.P. 2,476,069.

Fibres of a copolymer of 70-95% of vinylidene chloride and 30-5% of vinyl chloride or a vinyl ester of a monocarboxylic acid are treated for 1-15 sec. with cyclohexanone with or without methyl ethyl ketone and then immediately treated with water or steam.

C. O. C.

**Rendering Organic Materials Water-repellent.** M. E. Thayer and Dow Corning Corp. U.S.P. 2,474,704.

The materials are rendered hydrophobic by treatment with monomethyldiethoxysilane vapour. Subsequent



baking at 30–300°C. usually improves their moisture resistance. C. O. C.

**Figured Effects.** Bleachers' Assocn. Ltd., F. Farrington, A. E. Stubbs, and E. Hall. B.P. 630,172.

Figured effects are produced on cellulosic fabric by printing on a pattern with a non-resinous nitrogenous organic compound, having at least one long aliphatic chain, which on heating renders the fabric water-repellent, heating to develop water-repellency, and then treating firstly with sulphuric acid of parchmentising strength, secondly with caustic soda of mercerising strength, and finally repeating the acid treatment. The printed portions resist the acid and alkali treatments. C. O. C.

**Flameproofing.** Fine Spinners & Doublers Ltd., M. Cunningham, Bleachers' Assocn. Ltd., and W. Kershaw. B.P. 627,107.

A zinc boro compound is precipitated on yarn by double decomposition of aqueous solutions, of a zinc salt and a borate, the water-soluble salts are removed from it, and then the yarn is dried. It is then impregnated with an emulsion of polyvinyl chloride plasticised with an organic phosphate, dried, and heated to cause the polyvinyl chloride to form a film over it. Cloth made from such a yarn is air-permeable and has flameproof properties fast to washing and weathering. C. O. C.

**Pile Fabrics having Pattern Decorations.** Behr-Manning Corpn. B.P. 628,582.

Fibres are deposited on a hardenable adhesive coated on a backing sheet. While the adhesive is still soft several air jets play upon the surface, thus causing fibres in certain areas to lie in a different direction from the others. J. W. B.

**Resin-impregnated Glass Fibre Material.** Owens-Corning Fiberglass Corpn. B.P. 630,199.

Glass-fibre materials are impregnated with a low-pressure forming thermosetting resin with addition either to the resin or, as a pretreatment, to the fibres, of a silicate of general formula  $(CH_2:CR-CH_2O)_nSi$  ( $R = H, Alk, Ar, \text{ or } Hal$ ). Thus glass-fibre cloth is dipped in a 3% solution of tetramethylallyl silicate in xylene and air-dried to remove the solvent. It is then impregnated with a thermosetting styrene copolymer, built up to a laminate, and cured by heat and pressure. The product has improved strength, flexural, and water-resistant properties. J. W. B.

**Fastness to Alkaline Milling of Dyeings and Prints.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25. (XIV, p. 166.)

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

### PATENTS

**Pigmented Paper Stock.** R. T. Vanderbilt Co. Inc. and W. L. Craig. B.P. 628,603.

Highly pigmented cellulosic fibres, e.g. groundwood or chemical pulp, containing the pigment largely within the fibres and also on and around the fibres, are prepared by subjecting an aqueous suspension to the action of calcium chloride, at 15% concentration and in excess of the dry weight of fibre, for a sufficient time to form hydrated and gelatinised fibres, and adding a soluble salt, e.g. sodium carbonate, to precipitate finely divided calcium carbonate in and around the fibres, or sodium borate to precipitate calcium borate. Consistencies of 4–13% may be employed and excess alkali should be avoided to prevent darkening of the stock. Groundwood stock can be pigmented, with some loss in strength, up to 4 parts of pigment to 1 of dry fibre, and chemical pulp up to 2:1. Laminated sheets may be made with a liner prepared from the pigmented stock alone or mixed with ordinary stock. S. V. S.

**Coloration of Paper.** V. G. Morgan and I.C.I. Ltd. B.P. 630,463.

Brilliantly coloured papers of very high fastness to light are obtained by treating them at any stage of manufacture with a dye, particularly a phthalocyanine dye, containing quaternary ammonium or ternary sulphonium or isothiouonium salt groups, each of which is attached through a methylene radical to the carbon atom of an aromatic nucleus, e.g. the products obtained by the processes of B.P. 576,234, 576,270, 587,636, and 613,980 (cf. J.S.D.C., 62, 297, 327 (1946); 63, 304 (1947); 65, 461 (1949)). C. O. C.

**Diazotype Sensitised Papers having Cellulose Ether Sizing.** S. C. Slifkin and General Aniline & Film Corpn. U.S.P. 2,474,700.

Addition to the photosensitising solution of, or substitution of part or all of the surface sizing material by, cellulose ethers of general formula  $R-(CH_2)_n-O-Cell$  ( $R = OH \text{ or } COOH, n = 1-4$ , and  $Cell = \text{a cellulose nucleus}$ ) gives better, speedier, and more uniform penetration of the sensitising material into the paper. C. O. C.

**Washing Cellulose.** J. W. Allquist and Celanese Corpn. of America. U.S.P. 2,472,877.

Calcium, magnesium, sodium, and other cations adsorbed by cellulose from industrial water are removed by washing it with an ordinary industrial water brought to pH 2–5 with an inorganic acid so as to loosen and displace the cations and then washing out the displaced cations and the acid with demineralised water. C. O. C.

**Bleaching Mildewed Poplar Groundwood.** K. A. Craig and Paper Patents Co. U.S.P. 2,474,034.

A white fibre is obtained from poplar groundwood that has been attacked by fungi by bleaching it with a solution of alkaline hypochlorite, at pH 9–11 and 25–50°C., containing 7–15% available chlorine on the weight of the groundwood. After all the chlorine has been used sulphurous acid is added to the solution. C. O. C.

**Stable Cellulose Triacetate.** British Celanese Ltd. B.P. 627,861.

Stable cellulose acetate mouldable at high temp. without undergoing serious decomposition or discoloration is obtained by heating the primary acetate solution containing organic acid anhydride and free from water to 85–130°C. for 1–30 hr., the sulphuric acid catalyst having first been neutralised with magnesium acetate. W. G. C.

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

### PATENTS

**Water-soluble Hydroxymethylmelamine Condensates for Tanning Leather.** American Cyanamid Co. B.P. 628,818.

The products obtained by condensing a hydroxymethylmelamine or its copolymer with a hydroxymethylurea with an aminocarboxylic or aminosulphonic acid or an ammonium or alkali-metal salt of such an acid yield stable aqueous solutions useful for tanning hides and in the bleaching and filling of chrome- or vegetable-tanned leather. C. O. C.

**Tanning Leather, Protein Artifacts or Fibres, etc.** John R. Evans & Co. B.P. 628,989.

The material is treated simultaneously with resorcinol or pyrogallol and formaldehyde, a polymer of formaldehyde, or acet., croton-, benz-, or furfuraldehyde in aqueous medium at pH 0.3–3.0. The tanned materials show great improvement in qualities, particularly as regards the shrink test in boiling water. C. O. C.

**Tanning Leather.** John R. Evans & Co. B.P. 628,741.

Animal skins are treated with an aqueous solution containing not < 5% free melamine on the wet weight of the skins, as well as > 1 mol. of free formaldehyde per mol. of melamine, neither the melamine nor the formaldehyde having reacted at the start of tanning. Tanning is carried out for 3 hr. and gives a leather having a shrink test of at least 190°F. C. O. C.

## XIII—RUBBER; RESINS; PLASTICS

**Staining Problems associated with Rubber Chemicals.** J. Haworth and W. R. Pryer. *Trans. Inst. Rubber Ind.*, 25, 265–286 (Dec. 1949).

Nomenclature for the various types of staining associated with vulcanised rubber is suggested and compared with a recently proposed American system. An accelerated test based on the ultra-violet lamp is described, and the results are compared with those obtained in ordinary daylight. The effects on coloration and discoloration of the various ingredients of a rubber mix are described, viz. type of rubber, fillers, sulphur, accelerators, curing agents, retarders, antioxidants, softeners, plasticisers, peptisers, substitutes, reclaim, and blowing agents. With regard to accelerators, the effect of cure on coloration and discoloration is discussed, and the relation between finger-marking

and accelerator type outlined. Methods for testing staining by migration are described. This type of stain is usually due to antioxidants and can take place from rubber to a variety of other materials, e.g. cellulose acetate lacquers, cellulose nitrate enamels and lacquers, urea-formaldehyde enamels, rubber varnishes, wax finishes, and polyvinyl chloride. "Pinking" of textiles and papers is discussed. It is usually due to accelerators, and it has been shown that rubber compounds containing guanidines, aldehyde-amines, and thiocarbanilide can all cause pinking. The intensity of the pink stain increases with the state of cure, being at a maximum with optimum cures and overcures. Undercures tend to cause a yellow stain rather than a pink. This "pinking" is independent of light and thus different from the usual staining by migration. C. O. C.

## PATENTS

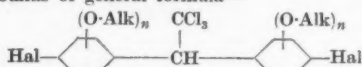
**Rubber Latexes containing Antioxidants.** Firestone Tire & Rubber Co. and J. C. Carl. B.P. 629,663.

Stable, concentrated dispersions of antioxidants in natural or synthetic rubber latexes are obtained by adding to the latter half their weight of an aqueous dispersion prepared by heating a mixture of the antioxidant and 5% of an ethanolamine soap, e.g. triethanolamine oleate, and dispersing this mixture in an equal weight of a 10% aqueous solution of a casein salt, e.g. ammonium caseinate. E. C.

**Plasticisers for Polyvinyl Halides.** B. F. Goodrich Co. B.P. 630,338.

Dialkyl phthalates in which each alkyl group has a branched chain and contains 6–12 C and the two alkyl groups together contain 12–18 C are good stabilisers for polyvinyl chloride, etc. and have the advantage of being more resistant to hot water than the straight-chain dialkyl phthalates. C. O. C.

**Plasticisers.** British Celanese Ltd. B.P. 627,710.  
Compounds of general formula—



( $n = 0, 1, \text{ or } 2$ ), e.g. di-*p*-chlorophenyltrichloroethane, are good plasticisers for cellulose derivatives, synthetic resins, etc. W. G. C.

**Non-toxic Phosphoric Ester Plasticisers.** British Celanese Ltd. B.P. 628,477.

Phosphoric esters having halogen in the *meta* or *para* position and of general formula—



( $n = 0, 1, \text{ or } 2$ ;  $m = 1-5$ ) are non-toxic plasticisers for cellulose esters and ethers. Tri-*p*-chlorophenyl phosphate is not claimed. W. G. C.

**Acrylic Polymers.** R. Hammond and I.C.I. Ltd. B.P. 628,150.

Soluble organic materials which polymerise on heating to give hard resins are made by treating a monohydroxy acrylic ester, e.g.  $\beta$ -hydroxyethyl methacrylate, with a polymethylol compound, e.g. hexamethylolmelamine, in presence of a polymerisation inhibitor. W. G. C.

**Styrene-*p*-Chloro- $\alpha$ -methylstyrene Copolymers.** Monsanto Chemical Co. B.P. 629,320.

The heat distortion point of polystyrene is raised by approx. 40°C. by forming copolymers containing 20–60% by weight of *p*-chloro- $\alpha$ -methylstyrene. W. G. C.

**Stabiliser for Vinyl Resins.** British Thomson-Houston Co. Ltd. B.P. 629,332.

Vinyl polymers are stabilised to the action of heat and light by lead trimethylsilanoxyde. W. G. C.

**Striping with Ketone Dye Solutions of Wires coated with Vinyl Resins.** R. J. Brown and Anaconda Wire & Cable Co. U.S.P. 2,474,088.

Use of dyes dissolved in liquid ketones neither affects the properties of the resin nor increases the diameter of the sheath and gives colourings which are not affected by moisture, oils, or handling. C. O. C.

**Hardening Proteinaceous Substances.** BX Plastics Ltd. and S. H. Pinner. B.P. 630,150.

Casein, zein, etc. are hardened by reaction with a hydroxymethylmelamine ether. C. O. C.

**Microporous Sheet Material.** J. J. Raymond, W. H. Lehnberg, and American Felt Co. U.S.P. 2,474,201.

A low-density wool felt is impregnated with latex, synthetic resin, etc., and then treated chemically or thermally so as to remove some or all of the wool and leave a product having the desired porosity, permeability, and capillary absorption properties. C. O. C.

**Polysiloxanes.** British Thomson-Houston Co. Ltd. B.P. 629,642.

Polysiloxanes obtained by hydrolysing a dimethyl-silicon dihalide are converted to elastic gums by treating with approx. 1% of an alkyl- or arylphosphoryl or -phosphonyl dihalide, e.g. phenylphosphonyl dichloride, for several days at 25°C. or several hours at 100°C. The products may be compounded and cured with a polymerisation catalyst in the usual way. E. C.

**Organic Pigments and Moulding Powders.** Calico Printers' Assn. Ltd., L. A. Lantz, A. Schofield, and E. Spinner. (IV, p. 156.)

**Adhesion of Rubber and Textiles.** E. M. Borroff and W. C. Wake. (X, p. 162.)

## XIV—ANALYSIS; TESTING; APPARATUS

**Colorimetric Determination within the pH Range 10–15—II.** N. Konopik and O. Leberl. *Sitzungsber. Öster. Akad. Wiss.*, 158, (3–4), 420–429 (1949).

The half-value stages and salt errors have been determined exactly for the indicators Neutral Blue R, Neutral Blue B, Fast Chrome Orange R, and Lanacyl Violet within the pH range 10–15, while the half-value stages have been graphically evaluated for the indicators Carbazole Yellow W, Chlorantine Light Blue GLN, and Coelestine Blue. H. H. H.

**Spectrophotometric Testing of D&C Violet No. 2 (Alizuril Purple SS).** M. Dolinsky. *J. Assocn. Offic. Agr. Chemists*, 31, 674–677 (1948); *Chem. Abs.*, 43, 7367 (10th Oct. 1949).

The spectrophotometric method eliminates the disadvantages of  $\text{TiCl}_3$  titration and of calculation from the N content. It is applicable in determining the dye content of commercial samples. C. O. C.

**Microanalytical Method for Azo Dyes.** L. V. P. Shkitin. *Zhur. Anal. Khim.*, 2, 231–235 (1947); *Chem. Abs.*, 43, 6948 (25th Sept. 1949).

The dye is split by action of a halogen, preferably  $\text{Br}_2$ , into a diazo component and a bromoazo component, which are then identified. The dye can be on a strip of filter-paper, sized paper, or yarn. The dyed material is moistened with distilled water and then treated with saturated bromine water. The diazo component is determined by coupling it with various azo components. To this end dimethyl ketone solutions, e.g. of resorcinol,  $\alpha$ - or  $\beta$ -naphthol, R-salt, or chromotropic acid, are applied to various spots on the dyed material, which is then exposed to  $\text{NH}_3$ . The diazo component is identified from the resulting colours. The bromoazo component is identified by fluorescent analysis in filtered ultra-violet radiation. Mixtures of azo dyes are separated by the Goppelsroeder method. C. O. C.

**Determining the Boiling Range of pseudoCumidine in FD&C Red No. 1.** K. A. Freeman and L. S. Harrow. *J. Assocn. Offic. Agr. Chemists*, 32, 127–129 (1949); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

A mixture of 100 g. of FD&C Red No. 1 in 2 litres of hot water and 10 g. NaOH was steam-distilled, 30%  $\text{NaHSO}_4$  soln. added dropwise until the red disappeared, and steam distillation continued until no more oil distilled. The distillate was extracted with four 20-ml. lots of ether, the extract washed with water, most of the ether evaporated in a steam-bath, and the residue dried over NaOH or KOH pellets. The residual solution was filtered into a semimicrofractionating apparatus, heated on a water-bath till ether-free, and further heated with a constant temperature bath to record the boiling range of the pseudocumidine. C. O. C.

**Spectrophotometric Analysis of D&C Red No. 19 (Rhodamine B).** M. Dolinsky. *J. Assocn. Offic. Agr. Chemists*, 32, 130–135 (1949); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

The absorption curve of a neutral or alkaline solution of purified D&C Red No. 19 showed a sharp peak at

553  $\pm$  2 m $\mu$ . with a "shoulder" at 520 m $\mu$ . In strongly acid soln. the peak shifted to 556 m $\mu$ . Beer's law is applicable to dilute ammonia solutions containing 1-5 mg. of dye per litre. The average extinction per mg./litre was 0.233  $\pm$  0.001 at 553 m $\mu$ . The extinction ratio  $E_{510 \text{ m}\mu}/E_{553 \text{ m}\mu}$  was 0.36  $\pm$  0.01. The data were applied to the determination of the dye in commercial samples. C. O. C.

**Report on Subsidiary Dyes in D&C Colours. D&C Red No. 6 or 7.** L. Koch. *J. Assocn. Offic. Agr. Chemists*, 31, 603-605 (1948); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

*p*-Toluidine was not recovered quantitatively from three certified samples of rosinated D&C Red No. 7, with and without adulteration, by the method described. C. O. C.

**Report on Spectrophotometric Testing—Analysis of Coaltar Colours: Extract D&C Orange No. 1.** R. N. Sclar. *J. Assocn. Offic. Agr. Chemists*, 31, 598-602 (1948); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

3.2-25.3 mg./litre solutions of the dye in chloroform, showing an absorption peak at 432  $\pm$  2 m $\mu$ , obey Beer's law. At this wavelength the average extinction per mg./litre is 0.0496 and the extinction ratio  $E_{420 \text{ m}\mu}/E_{450 \text{ m}\mu}$  is 1.10  $\pm$  0.005. The pure dye content of a sample can be determined by comparison with these data. C. O. C.

**Pure Dye in Lakes and Pigments.** K. A. Freeman. *J. Assocn. Offic. Agr. Chemists*, 31, 595-598 (1948); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

Samples of the calcium lake of D&C Red No. 7, the sodium lake of D&C Red No. 8, the sodium salt of D&C No. 10, and the calcium lake of D&C Red No. 31 were analysed by the official method. The results for different workers were consistent, being high or low for all their results, probably caused by variations in the standard  $\text{TiCl}_3$  soln. Back titration at the option of the analyst to avoid uncertainty as to the true end-point is suggested. C. O. C.

**Determination of Lead in Lakes of Coaltar Colours.** L. S. Harrow. *J. Assocn. Offic. Agr. Chemists*, 31, 677-683 (1948); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

Precipitating the lead as PbS and extracting with dithizone solution gave an average recovery of 99% after 20-150 p.p.m. had been added to the alum lake of D&C Blue No. 1. Alkaline earth samples were fused with excess sodium or potassium carbonate and then extracted with dithizone. Recovery averaged 98% for samples containing 40-200 mg. Pb per 2 g. of the barium lake of D&C Red No. 9. C. O. C.

**Non-volatile Unsulphonated Amine Intermediates in Coaltar Colours.** L. S. Harrow. *J. Assocn. Offic. Agr. Chemists*, 31, 594, 595 (1948); *Chem. Abs.*, 43, 7231 (25th Sept. 1949).

Extraction with ether and titration with  $\text{TiCl}_3$  are used for determining *p*-nitroaniline in D&C Black No. 1. Recoveries of > 95% are obtained from samples containing 0.2-0.4% of *p*-nitroaniline. C. O. C.

**Moisture Determination of Textiles by Electrical Meters—II.** R. K. Toner, C. F. Bowen, and J. C. Whitwell. *Text. Research J.*, 19, 1-8 (Jan. 1949).

Additional experiments on two moisture meters, (a) the Hart and (b) the Steinlite, illustrating the effects of temperature, dye, salt concentration, and fibre variation have been made. The results show the need for calibrating the material and specifying the conditions of use. Drying the textile material by heating causes a deviation from the calibration curve for that material with a particular meter, although if the difference is small the slight loss in precision may be permissible. The temperature at which measurements are made may cause deviations in the calibration curves. For greater accuracy the meters should be used at the temperature for which they are calibrated. Dyes and type of fibre influence the readings obtained in the direction of a higher regain than is actually present. Salts have a similar effect. P. C.

**New Method of sectioning Synthetic Fibres with the Ultra-microtome for Examination with the Electron Microscope.** M. D. Earle and J. A. Minkin. *Text. Research J.*, 19, 36-41 (Jan. 1949).

**Determination of small amounts of Pentosan in Cellulose Materials.** T. Kleinert. *Sitzungsber. Öster. Akad. Wiss.*, 158, (3-4), 346-355 (1949).

Earlier work on  $\alpha$ -celluloses is now confirmed, viz. that they contain no appreciable amount of pentosan. By distillation of cellulose materials with 13% HCl by the Tollens procedure, the characteristic product is hydroxymethylfurfural, which was established by bromometric and absorptiometric determinations. This compound inhibits the precipitation of small amounts of furfural by means of barbituric acid. H. H. H.

**Gravimetric Determination of Pentosan in Cellulose Materials by Barbituric Acid.** T. Kleinert. *Sitzungsber. Öster. Akad. Wiss.*, 158, (3-4), 356-358 (1949).

It is shown that in the determination of small amounts of pentosan in cellulosic materials by barbituric acid precipitation, the Tollens distillation procedure forms hydroxymethylfurfural from the glucose residues of cellulose, which may completely inhibit the precipitation. Agreement has been found for furfural values from cellulose materials exceeding about 2.5% between the bromometric data and those obtained by barbituric acid precipitation. H. H. H.

**Identification of the End Amino Groups of Wool by means of their 2:4-Dinitrophenyl Derivatives.** W. R. Middlebrook. *Nature*, 164, 501-502 (17th Sept. 1949).

The 2:4-dinitrophenyl derivatives of the amino acids having free  $\alpha$ -amino groups in wool have been identified, using Sanger's technique (*Biochem. J.*, 39, 507 (1945)), as valine, alanine, glycine, threonine, serine, glutamic acid, and aspartic acid. For quantitative determination, it is found most convenient to run the ether-soluble fraction on a 2-g. silica gel column buffered at pH 6.0 with ether as solvent, which achieves individual separation of the glycine, threonine, serine, glutamic, and aspartic derivatives in one operation, the valine and alanine moving as a fast band together with the decomposition products containing 2:4-dinitroaniline and 2:4-dinitrophenol. H. H. H.

**Re-examination of Present Wetting Tests.** S. M. Edelstein and C. Z. Draves. *Amer. Dyestuff Rep.*, 38, P343-P347, P352 (18th April 1949).

The present wetting tests based on the relation between concentration of wetting agent and time of sinking, for a weighted skein of cotton or canvas disc, are shown to depend on the conditions chosen unless the comparison is between wetting agents with the same chemical constitution. They are consequently of value only under that condition or where the comparison is carefully related to the particular use for which the assessment is required. W. J. M.

**Tristimulus Computation in the Dyestuff and Textile Field.** I. H. Godlove and General Aniline & Film Corp. *Anal. Chem.*, 21, 535 (April 1949).

The tristimulus integrator described by Davidson and Imm has been found, because of its high precision and saving of time, to yield many results of interest to the textile-dyeing field not conveniently obtained previously. It permits statistical analyses, e.g. for obtaining a measure of unevenness (non-uniformity) of dyeings. The average differences between the trichromatic coefficients  $x$  and  $y$  for a.m. and p.m. repeats on six red wool dyeings were 0.0004. This includes the overall errors due to the spectrophotometer itself, the positioning of samples, and the integrator. Other work indicates that the precision is adequate for small-difference colorimetry. Work has been done on liquid and film filters to yield analyses for night lighting as well as daylight. Results contrasting additive mixing on a union (cotton-wool) dyeing and the subtractive mixture of dye solutions, were shown; also studies on "dyer's brightness", which is related to saturation. The computer has also been used to follow the striking changes of colour due to aggregation of dye molecules in solution; this and other dye phenomena were illustrated. M. E. W.

**Assessment of Fastness Properties.** H. Ria. *Textil-Rund.*, 4, 396-400 (Nov. 1949); *Teintex*, 14, 459-463 (Nov. 1949).

A review of the development of standard methods of assessing fastness properties of coloured textiles. Standard



testing methods developed by the D.E.K., S.D.C., I.C.I., and A.A.T.C.C. are discussed. A French Textile Institute was founded in 1946 and took up the establishment of standard testing methods for France. In 1949 collaboration between French and Swiss workers commenced in order to evolve mutually acceptable testing methods for assessing fastness to light, washing, alkaline milling, carbonising, water, sea-water, hot pressing, and rubbing.

B. K.

**Assessment of Fastness to Light of Textiles.** P. Rabé. *Melliand Textilber.*, 30, 470-472 (Oct. 1949).

A survey of European and American methods of assessing the fastness to light of dyed textiles by standard methods.

B. K.

**Fastness to Washing of Coloured Textiles.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A2521. *Textil-Rund.*, 3, 356-357 (Oct. 1948).

Three standard methods for testing the fastness to washing of coloured textiles are proposed—

*Grade A*, for cotton, linen, viscose, wool, silk, acetate rayon, and nylon—5 g. of soap per litre, for 30 min. at 40°C.

*Grade B*, for cotton, linen, viscose, and wool (for fast-to-washing and fast-to-milling shades)—5 g. of soap and 2 g. of soda per litre for 30 min. at 60°C.

*Grade C*, for boil-fast shades on cotton and linen—5 g. of soap and 2 g. of soda per litre for 30 min. at 90°C.

Wool dyeings are first neutralised by two treatments in 10 g. of sodium acetate per litre for 15 min. at 20°C. The washing tests are carried out in a 50:1 liquor ratio by hand, in the Launderometer or in Geigy's apparatus described in *Textil-Rund.*, 2, 323 (1947).

B. K.

**Fastness of Dyeings to Carbonising.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A2573. *Textil-Rund.*, 4, 299 (Aug. 1949).

A standard method for assessing fastness to carbonising entails treatment for 15 min. at 15-20°C. in 7.4%  $\text{H}_2\text{SO}_4$  or 7.4%  $\text{AlCl}_3$  followed by drying and neutralisation under standard conditions.

B. K.

**Fastness to Alkaline Milling of Dyeings and Prints.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A2571. *Textil-Rund.*, 4, 298 (Aug. 1949).

A standard method for assessing fastness to milling entails the use of the Launderometer or other apparatus. 10 g. soap per litre for 30 min. at 40°C. represents a light milling and 50 g. soap and 10 g. soda per litre for 2 hr. at 40°C. a severe milling.

B. K.

**Light Fastness of Coloured Textiles.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A2501. *Textil-Rund.*, 3, 313-314 (Sept. 1948).

Fastness to light of coloured textiles is tested by exposure against eight dyed standards on wool—

1. 0.8% Brilliant Wool Blue FFR extra (IG)
2. 1% Brilliant Wool Blue FFB extra (IG)
3. 1.2% Brilliant Cyanine 6 B (Ciba)
4. 1.2% Supramine Blue EG (IG) or 1.1% Polar Blue G conc. (Gy)
5. 1% Alizarine Light Blue R (S)
6. 3% Alizarine Light Blue 4GL (S)
7. 3% Indigosol 06B (DH)
8. 3% Indigosol AGG = Anthrasol AGG (IG)

Daylight exposures are preferable, and as an alternative the use of the Fadeometer is recommended.

B. K.

**Testing the Moth-resistance of Wool Textiles.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A3001. *Textil-Rund.*, 4, 65-66 (Feb. 1949).

Full details are given of the Swiss (S.V.M.T.) standard method for testing the moth-resistance of wool textiles. The test consists in measuring the loss in weight of samples which are charged with larvae and stored, together with control samples, under specific conditions. A material is designated mothproof if its loss in weight is not greater than 12% of the loss in weight of the control material.

F. A.

**Water Fastness of Coloured Textiles.** Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A2511. *Textil-Rund.*, 3, 432 (Dec. 1948).

The fastness to water of coloured textiles is tested by wetting out the material in water at 20°C., and then making a plait or roll with suitable undyed materials which is placed in a test-tube 18 mm. in diameter and covered with distilled water, liquor ratio 6:1. The tests are left for 16 hr. at 15-20°C., hydroextracted, opened up, and air-dried at 60°C. A one-hour test is suggested for dyes of poor fastness to water.

B. K.

**Fastness to Sea-water of Dyeings and Prints.**

Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A2512. *Textil-Rund.*, 4, 297 (Aug. 1949).

A standard method for assessing fastness to sea-water entails treatment under specified conditions in water containing 30 g. of sodium chloride per litre.

B. K.

**Evaluation of Levelling Agents.** D. H. Gunther. *Amer. Dyestuff Rep.*, 38, P236-P238 (7th March 1949).

A number of methods which have been proposed to evaluate the efficiency of levelling agents in dyeing cellulosic fibres and wool are listed, without criticism. Most depend on the comparison of dyeings carried out under various conditions in the presence and absence of the agent, using dyes known to possess poor levelling properties; or on the efficiency of equalising dyed and undyed fabric.

W. K. R.

**Microbiological Degradation of Wool. I—Sulphur Metabolism.** W. H. Stahl, B. McQue, G. R. Mandels, and R. G. H. Siu. *Arch. Biochem.*, 20, 422-432 (1949); *Chem. Abs.*, 43, 8142 (1949).

Degradation of wool by the fungus *Microsporium gypseum* was followed analytically with respect to S by use of the shake-culture technique. With time the S in the solid residue aliquot decreased while sulphate S increased, this difference levelling off after 13 days and remaining constant. The cystine S in the filtrate rose to a maximum along with the sulphate S until the 11th day, after which it decreased, becoming practically absent on the 21st day. Inorganic sulphate was an end-product of the decomposition of wool by fungi. *M. gypseum* caused fission of the C-S linkage in methionine with production of  $\text{CH}_3\text{SH}$ . Methionine, unlike cystine, cysteine, and  $\text{Na}_2\text{SO}_4$ , caused definite inhibition of fungal growth at high concentrations, probably due to formation of the toxic  $\text{CH}_3\text{SH}$ .

C. O. C.

**Mothproofing Tests.** O. Wälcchi. *Textil-Rund.*, 4, 247-253 (July 1949).

For testing mothproofing, four tests each using 25 mothgrubs 3-5 mm. long are used, this length ensuring that the grubs are in the middle stage of their development, when they are at their hungriest. A large portion of the surface of the test sample should be coated with bait, but there must always be a ring of unbaited material left completely round the edge of the sample. This is necessary because up to a certain point (an area 20 mm. in diameter) increase in size of baited area results in increase in frass, this increase being much larger in the case of untreated material compared with mothproofed material. The bait must never be on the edges, as the grubs feed much more easily at the edges than on the surface of cloth. The amount of damage (judged by frass produced) varies greatly with the type of fabric, hard smooth cloths being less readily attacked than those of softer, raised fabrics, and with tightly spun yarns or hard cloths there is less bitten-off fibre in the frass. Thus the control should not be a standard fabric but one as similar as possible to the sample under test. The best way of expressing the results of the tests is to pass as mothproof any sample the frass from which is not more than 12% of that from the control.

C. O. C.

**Damage to Printed Rayon [by Silverfish].** E. Laibach. *Melliand Textilber.*, 30, 295-299 (July 1949).

Silverfish (*Lepisma saccharina* L.) attacks printed viscose or cuprammonium rayon to a greater extent than unprinted rayons, but the actual dye has no influence on the degree of damage. Thickening agents are difficult to remove completely despite careful washing-off, but apart from starch, no increased attack by silverfish is caused.

B. K.



# Attack of Rayons by Silverfish. E. Laibach, *Melliand Textilber.*, 29, 397-401 (Dec. 1948).

Silverfish attack viscose and cuprammonium rayons by feeding on them, but do not touch acetate rayon or the untreated cellulose from which the rayons are prepared. Experiments with a series of celluloses degraded to various extents show that the decomposition must reach a certain stage before the material can be assimilated by silverfish. This explains the attack of viscose and cuprammonium rayons, but with these materials the degradation of the cellulose has not reached the stage at which it provides a perfect food for the silverfish. F. A.

# Fungi concerned in Fibre Deterioration. I—Their Occurrence. P. B. Marsh and K. Bollenbacher. *Text. Research J.*, 19, 313-324 (June 1949).

A review of the literature on the common types of fungi commonly found growing on cellulosic textile fibres under particular conditions, chiefly above ground. Resistance of the fungus to sunlight is believed to be important in determining which types grow on fibres in different conditions of exposure. Temperature and moisture requirements of different fungi are also important. There are 60 references to the literature. P. C.

# Fabric Mildew Resistance Tests with Organisms tolerant toward Copper and Mercury. P. B. Marsh. *Amer. Dyestuff Rep.*, 38, 436, 451-452 (30th May 1949).

Grey duckcloth was treated with copper naphthenate, copper oleate, copper "tallate", and copper hydrogenated resinate at rates equivalent to 0.1-0.8% copper on the fabric. Certain moulds were decidedly more copper-tolerant than others. Copper naphthenate was by far the most effective agent. Similar results were obtained with pyridylmercury stearate. W. J. M.

# Corrosive Effects of Fungicides. ORR 185/49\* (PB 4088).

Copper naphthenate used as a fungicide on textiles may accelerate the corrosion of aluminium or zinc with which they are in contact at high humidity, but exerts a protective influence on brass. Zinc naphthenate acts as a corrosion inhibitor to steel, zinc, and aluminium. Salicylanilide and dihydroxydichlorodiphenylmethane are inert. C. O. C.

\* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see J.S.D.C., 66, 53 (Jan. 1950).

# Tests of Shirts, Flannel, Shrinkproof Treatment. U.S. Quartermaster Board. ORR 166/49\* (PB 32,845).

The results of tests made on flannel shirts treated by several shrinkproofing treatments are given. Shrinkage and accelerated, comparative and normal wear tests are described. C. O. C.

\* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see J.S.D.C., 66, 53 (Jan. 1950).

# Flammability of Consumer Textiles. G. S. Buck, Jr. *Amer. Dyestuff Rep.*, 38, P78-P84 (24th Jan. 1949).

A series of interlaboratory tests in which the flammability of textiles was evaluated by two methods, viz. the A.A.T.C.C. inclined test and the N.B.S. horizontal test, have shown that with each method the results obtained by various laboratories differ significantly and that a precise determination of flammability is impossible. Although both tests demonstrate the hazard of long-pile fabrics, they do not always distinguish other known hazardous fabric types, and neither is sufficiently accurate to be adopted as a legal standard. The inclined test is preferred and may be of use as a guide in the production of clothing fabrics with a minimum hazard. A number of criticisms of the tests are made, along with recommendations for modifications in procedure and in interpretation of results. W. K. R.

# Ploche Colour System. W. E. K. Middleton. *Canadian J. Res.*, 27F, 1-21 (Jan. 1949).

The Ploche colour system consists of 1248 painted cards, the colours being produced by systematic pigment mixtures. There are 26 hues, with six chrome levels and eight value levels in each. The Munsell book notation of each colour is given, and the advantages and disadvantages of the system are pointed out. A. S. F.

# Artificial Colour Standards for Methyl Yellow and Methyl Orange. M. L. Nichols and B. L. Ingram. *Anal. Chem.*, 20, 1188-1191 (Dec. 1948).

From a consideration of the absorption spectra of potassium dichromate, ammonium cobalt sulphate, mixtures thereof, and Methyl Yellow and Orange at various pH values, it is shown that no mixture of the two salts can provide a spectrally-identical colour match for the two indicators at useful pH values corresponding to titration end-points, for use as artificial permanent colour standards. However, two visually matched standards are derivable from suitable mixtures, viz. 10 ml. of 0.002 M. dichromate plus 30 ml. of 0.2 M. cobalt salt diluted to 100 ml. to match 0.2 ml. of 0.1% Methyl Yellow in 100 ml. at pH 3.8, and 20 ml. of the dichromate plus 27 ml. of the cobalt salt solution diluted to 100 ml. to match 0.3 ml. of 0.1% Methyl Orange in 100 ml. at pH 4.0. These two artificial standards may be used in titrations only under daylight conditions. An examination of their colours with tristimulus filters and an approximated Judd formula shows that they agree with the values for the indicators much more closely than does an earlier mixture of the same two salts suggested by Böttger for Methyl Yellow comparison, especially in chromaticity or quality, but show some difference in brightness, which difference is not diminished by any variations in concentration without adversely affecting chromaticity matching; the Böttger mixture differs even more in brightness from the indicator. In visual comparisons, this residual brightness difference is not apparent. H. I. S.

# Consumer Complaints from New Fabrics and Finishes. L. G. Johnston. *Amer. Dyestuff Rep.*, 38, P65-P66, P76-P77 (24th Jan. 1949).

Examples are given of defects arising in laundering which are attributable to faulty manufacture or to the use of unsuitable textile materials, dyes, and finishes. These include relaxation shrinkage due to lack of pre-shrinking, the shrinkage of vinyon at moderate temperatures, tendering by certain vat dyes, surface prints which are removed by abrasion, and crease-resisting resins which retain chlorine. W. K. R.

# Proposal for Specifying the Stability of Coloured Materials to Radiant Energy. E. M. Lowry. *Amer. Dyestuff Rep.*, 38, 543-546 (July 1949).

It is suggested that fading be expressed as the area between the percentage transmission curves before and after fading. If the difference in total transmission were taken as the criterion, this would indicate no fading in the case of a change in colour but no change in total transmission. W. J. M.

# Some Properties of Acidic Oxycellulose. K. S. Bhujang and G. M. Nabar. *J. Sci. Ind. Research (India)*, 8B, 103-110 (1949); *Chem. Abs.*, 43, 8672 (10th Nov. 1949).

An approximate relationship between Methylene Blue absorption and carboxyl content exists when the absorption is determined under constant specific conditions. C. O. C.

# Photosensitisation by Vat Dyes. C. H. Bamford and M. J. S. Dewar. *Nature*, 163, 214 (5th Feb. 1949).

Certain vat dyes, which accelerate the tendering of cellulose by light, have been found to initiate the autoxidation of tetralin, and the polymerisation of styrene. When a number of dyes are arranged in order of activity for the autoxidation reaction, the order is similar to that for the tendering activities of the dyes on cellulose. Both reactions probably result from the formation of radicals by removal of hydrogen atoms from the substrate by the excited dye. The relative activities in the photopolymerisation reaction are not in the same order, and a direct energy transfer may be involved in this case. The quantum efficiency of the sensitisation reaction has been calculated for Caledon Golden Yellow GK, anthanthrone, and Caledon Red BN. A. S. F.

# Accelerated Oxidation of Cotton Cellulose in presence of Reducing Substances—I. G. D. Joshi, S. H. Mhatre, and G. M. Nabar. *Proc. Indian Acad. Sci.*, 29A, 277-287 (1949); *Chem. Abs.*, 43, 8671 (10th Nov. 1949).

The oxidation potentials of NaOCl soln. at 30°C. are given for pH 9.13-4.95; the values are higher at 30° than at 20°C.; the differences in the potentials become more

and more marked with reduction in pH. A correction of  $\text{pH} \times 0.06$  v. to the measured potentials at 30°C. does not show a maximum value over the pH region examined. Sharp change in the direction of the pH-corrected oxidation potential curve occurs at about the same pH as that at which a maximum is obtained at 20°C. There is no similarity between the corrected oxidation potential-pH curve at 30°C. and a curve showing the relation between the oxygen uptake or fluidity and pH at 30°C. C. O. C.

**Conditions of Temperature and Humidity in the Fadeometer.** G. Nordhammar. *Amer. Dyestuff Rep.*, 38, 571-574, 593 (Aug. 1949).

The temperature and humidity of the air in the Fadeometer and at the surface of the dyed fabric have been measured by means of thermocouples. The air temperature varied markedly according to the number of samples in the Fadeometer (with 21 samples it was 55-90°C., according to the closeness to the arc, and with 11 samples the temperature dropped to 35-45°C.). The surface temperature of the samples fluctuated at about 90°C. for black unbleached wool, and was a few degrees lower for the white sample. The relative humidity was found to be 10%. The use of wet wicks for humidification is fundamentally useless, as the air is passed over the wicks at room temperature. Suggestions for improving the conditions in the Fadeometer by means of baffles are made.

W. J. M.

**Water-absorbency Apparatus.** E. C. Jackson and E. R. Roper. *Amer. Dyestuff Rep.*, 38, 397-401 (16th May 1949).

An apparatus designed to measure the rate of water absorption by cloth consists essentially of a capillary tube connected to the water source under a porous plate, on top of which is placed the cloth being examined. The rate of flow of water in the capillary tubing is determined visually, thus eliminating the necessity of weighing. Some typical absorption curves of towelling are illustrated, and the relative importance of various factors which may affect the results, such as atmospheric humidity and pressure on the sample, is assessed.

A. S. F.

**Testing Apparatus for the Evaluation of Fire-resistant Textiles.** B. C. Rowley and M. Sonnino. *Amer. Dyestuff Rep.*, 38, 201-204 (7th March 1949).

Details are given of the construction of an apparatus for testing the flame resistance of fabrics in the vertical, horizontal, and 45° inclined positions, combining ease of operation with greater reproducibility. Improved features include the use of permanently located burners with attached pilot lights, the height of the flame being regulated by gas pressure and its duration automatically controlled by an electric timing device.

W. K. R.

PATENTS

**Measuring Humidity.** E. Jones. B.P. 625,189.

A device responsive to changes in humidity consists of a piece of material the volume of which is dependent upon its moisture content and which has electrical pick-off means associated with it to provide an electrical indication or signal dependent upon at least one dimension of the material. One way of doing this is to wind a single-layer coil of fine resistance wire upon a thin cylindrical former of regenerated cellulose sheet, to which it is secured by Canada balsam or cellulose acetate cement, the ends of the coil being connected to a Wheatstone bridge circuit.

C. O. C.

**Determining the Strength of Aqueous Solutions of Anionic Compounds or Cationic Quaternary Ammonium Compounds.** F. J. Cahn and Emulsol Corpn. U.S.P. 2,471,861.

The concentration of dilute aqueous solutions of (a) cationic quaternary ammonium compounds containing a chain of > 11 carbon atoms, e.g. cetyltrimethylammonium bromide, or (b) anionic compounds containing an uninterrupted carbon chain of > 11 carbon atoms and a sulphonate or sulphate radical, e.g. sodium lauryl sulphate, is determined by adding a little dichlorofluorescein to a standard volume of the solution and then titrating with a dilute aqueous solution of known concentration of a compound belonging to (b) or (a). The pink colour given by the fluorescein when the solution is viewed in transmitted light disappears at the equivalence point. This

colour change is more readily seen, and the equivalence point more sharply perceived, if a water-immiscible organic solvent, e.g. ethylene dichloride or chloroform, is added to the test sample. The colour changes are reversible, making back-titration readily feasible.

C. O. C.

**Testing for Acetone.** Denver Chemical Manufacturing Co. and A. Grant. B.P. 623,821.

A mixture of 1% of powdered anhydrous sodium nitroprusside, 49.5% of granular anhydrous sodium carbonate, and 49.5% of granular anhydrous ammonium sulphate becomes immediately coloured if a drop of a solution containing acetone is applied to it, the colour deepening with time. The colour varies from light green → light violet → medium violet → deep violet → deep purple-blue depending on the concentration of the acetone. The method may be used for qualitative estimations by comparing the colour after one minute with a range of known standards.

C. O. C.

**Determining the "Mileage" Characteristic of Printing Inks.** W. F. Talbot, R. Buchdahl, and Sun Chemical Corpn. U.S.P. 2,477,776.

The amount of an ink required to produce a desired coverage or required to make a given number of impressions can be ascertained by adding a radioactive substance to the ink and determining the radioactivity of the printed surface.

C. O. C.

**Adhesion of Rubber and Textiles.** E. M. Borroff and W. C. Wake. (X, p. 162.)

XV—MISCELLANEOUS

**Chemical Periodicals in the Dye and Textile Industries.** F. S. Boig and W. J. Fitzpatrick, Jr. *Text. Research J.*, 19, 325-329 (June 1949).

A statistical analysis has been made of articles on dyeing and textiles appearing in chemical and textile periodicals with the object of determining the relative importance of individual publications, the countries leading in the field of textile research, the need for chemists to know more than one language, etc. The analysis is based on a review of articles abstracted in the Dyes and Textiles Section of *Chemical Abstracts* for the years 1937, 1942, and 1947.

P. C.

**Tetrahydrofurfuryl Acetate Solutions of Eosin for Colouring Lipsticks and Rouges.** E. S. Lower. *Amer. Perfumer Essent. Oil Rev.*, 53, 121-123 (1949); *Chem. Abs.*, 43, 9365 (25th Nov. 1949).

Eosin forms a 28% solution in tetrahydrofurfuryl acetate, and formulae for its use in lipsticks and cream rouge are given.

C. O. C.

**Mercury Exposure in the Fur-felt Hat Industry.**

A. R. Smith, L. Goldwater, W. J. Burke, and S. Moskowitz. *N.Y. State Dept. Labor, Monthly Rev., Dir. Ind. Hyg. & Safety Standards*, 28, (5), 17-20; (6), 21-24 (1949); *Chem. Abs.*, 43, 8688 (10th Nov. 1949).

Tests carried out in a hat-manufacturing and in a fur-cutting plant showed that in the former exposure was principally to mercury vapour while in the cutters it is wholly to mercury-containing dust except in closed unventilated rooms. Of 213 men exposed to mercury vapour in the backshop of the hat manufacturers 39.9% showed evidence of chronic mercurialism.

C. O. C.

**Hyperthyroidism and Chronic Mercury Poisoning.** G. Baldi. *Med. lavoro*, 40, 113-124 (1949); *Chem. Abs.*, 43, 8689 (10th Nov. 1949).

Of 840 workers in a felt hat factory 21.3% suffered from mercurialism. Thyroid disease was found in 56 of them, but no correlation between mercury poisoning and thyroid affection was found.

C. O. C.

PATENTS

**Halogenated Fluoresceins for Colouring Cosmetics.** S. Gottfried. B.P. 629,102.

A halogenated fluorescein dissolved in a tetrahydrofurfuryl ester is used for colouring lipsticks or other cosmetics.

C. O. C.

**Chemically Coating Aluminium to receive Dyes.** O. L. Shawcross and Aluminum Co. of America. U.S.P. 2,466,971.

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